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LECTURES IN APPLIED MATHEMATICS

Proceedings of the Summer Seminar, Boulder, Colorado, 1960

VOLUME I

LECTURES IN STATISTICAL MECHANICS

By G. E. Uhlenbeck and G. W. Ford with E. W. Montroll

VOLUME II

MATHEMATICAL PROBLEMS OF RELATIVISTIC PHYSICS

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VOLUME III

PERTURBATION OF SPECTRA IN HILBERT SPACE

By K. O. Friedrichs

VOLUME IV

QUANTUM MECHANICS

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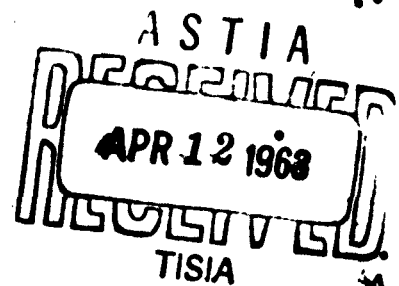
LECTURES IN APPLIED MATHEMATICS

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VOLUME I

by

G. E. UHLENBECK and G. W. FORD

with

E. W. MONTROLL

Mark Kac, *Editor*

The Rockefeller Institute

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by
G. E. UHLENBECK
THE ROCKEFELLER INSTITUTE

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WITH AN APPENDIX ON
Quantum Statistics of Interacting Particles
by
E. W. MONTROLL
RESEARCH CENTER, INTERNATIONAL BUSINESS MACHINES CORPORATION

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NA

Foreword

This is the first of a series of four volumes which are to contain the Proceedings of the Summer Seminar on Applied Mathematics, arranged by the American Mathematical Society and held at the University of Colorado for the period July 24 through August 19, 1960. The Seminar was under the sponsorship of the National Science Foundation, Office of Naval Research, Atomic Energy Commission, and the Office of Ordnance Research.

For many years there was an increasing barrier between mathematics and modern physics. The separation of these two fields was regrettable from the point of view of each—physical theories were largely isolated from the newer advances in mathematics, and mathematics itself lacked contact with one of the most stimulating intellectual developments of our times. During recent years, however, mathematicians and physicists have displayed alacrity for mutual exchange. This Seminar was designed to enlarge the much-needed contact which has begun to develop.

The purpose of the Seminar was primarily instructional, with emphasis on basic courses in classical quantum theory, quantum theory of fields and elementary particles, and statistical physics, supplemented by lectures specially planned to complement them. The publication of these volumes is intended to extend the same information presented at the Seminar to a much wider public than was privileged to actually attend, while at the same time serving as a permanent reference for those who did attend.

Following are members of a committee who organized the program of the Seminar:

> Kurt O. Friedrichs, Chairman
> Mark Kac
> Menahem M. Schiffer
> George E. Uhlenbeck
> Eugene P. Wigner

Local arrangements, including the social and recreational program,

were organized by a committee from the University of Colorado, as follows:

Charles A. Hutchinson
Robert W. Ellingwood

The enduring vitality and enthusiasm of the chairmen, and the cooperation of other members of the university staff, made the stay of the participants extremely pleasant; and the four agencies which supplied financial support, as acknowledged on the copyright page, together with the Admissions Committee, consisting of Bernard Friedman, Wilfred Kaplan, and Kurt O. Friedrichs, Chairman, also contributed immeasurably to the successful execution of the plans for the Seminar.

The Seminar opened with an address given by Professor Mark Kac, Department of Mathematics, Cornell University, on the subject "A Mathematician's Look at Physics: What Sets us Apart and What May Bring us Together." Afternoons were purposely kept free to give participants a chance to engage in informal seminars and discussions among themselves and with the distinguished speakers on the program.

Editorial Committee

V. BARGMANN
G. UHLENBECK
M. KAC, CHAIRMAN

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Preface

These lectures were given by one of us (G. E. U.) as a part of the summer symposium in theoretical physics, which was organized by the American Mathematical Society at the University of Colorado in the summer of 1960. The lectures are printed here almost in the same form as they were presented, which explains the rather colloquial style and the perhaps excessive use of the first personal pronoun. This last feature does *not* mean that the content of the lectures is due only to the first author. All lectures were thoroughly discussed and prepared by both of us, and most of the developments for which some originality may be claimed are the result of the collaboration of the two authors during many years.

The purpose of the summer symposium was to acquaint a group of mathematicians with some of the basic problems in present-day theoretical physics, hoping that this would stimulate a more intense collaboration. In our opinion such a collaboration would be especially valuable in statistical mechanics, since here many of the unsolved problems can be formulated precisely and are of a technical mathematical nature. Furthermore, because of the lack of exact knowledge of the intermolecular forces, one is usually more interested in the explanation of the qualitative features of the macroscopic phenomena than in the precise quantitative prediction of the macroscopic quantities. This qualitative aspect of the theory should appeal to the mathematician while for the physicist it is often a real difficulty. Since the facts are so well known the latter is often tempted to be satisfied with more or less uncontrolled approximations based on intuitive arguments. These are often very valuable, but usually they do not provide, so to say, a foothold for a rigorous mathematical treatment. In our opinion such a treatment is especially needed in statistical mechanics, and to provide it is the real challenge of the subject.

We have therefore stressed as much as possible the logical structure of the theory, and we have always tried to indicate the mathematical gaps which remain in the argument. In addition we have tried to start from the beginning and to avoid as much as possible the phrase: it can be shown. Proofs are often put in the notes at the end of each chapter together with references to the literature. We hope that as

a result the book can be used as a short but self-contained introduction to the subject, although we realize that it will have to be used with tact, since the textbook-like chapters alternate with chapters describing work still in progress.

To achieve, even only approximately, these rather conflicting goals, it soon became clear to us that we had to limit the field considerably. Not only have we restricted ourselves to the simplest possible physical systems (namely mono-atomic gases) but even for these systems we could only discuss a few characteristic problems. The most severe limitation we had to impose was the restriction to the classical theory. This is fortunately somewhat mitigated by the two lectures Dr. E. Montroll gave, which are reproduced in the Appendix. Here an account is given of some of the recent developments in quantum statistics to which Dr. Montroll himself has made such important contributions.

In one respect we did not want to limit ourselves. It is often customary either to consider only the statistical problems for the equilibrium state (sometimes called statistical thermodynamics), or to concentrate on the explanation of the irreversible and transport phenomena (sometimes called kinetic theory). It seems to us that such a limitation gives a distorted view of the subject, and that one should try to give a unified treatment both of equilibrium and non-equilibrium statistical mechanics. We have therefore devoted six lectures (reproduced in the first three chapters) to equilibrium problems and six lectures (reproduced in Chapters 4–7) to non-equilibrium problems, and we have attempted to point out at least the conceptional connections between the two fields.

Finally there remains the pleasant duty to thank in the first place Professor Mark Kac for all the help and advice he has given us. If these lectures would inspire one other mathematician of the calibre of Professor Kac to work on the problems of statistical mechanics the symposium would have more than justified itself! The reader would also be well advised to read in parallel with these lectures the third chapter in the book *Probability and Related Topics in Physical Sciences*, by Professor Kac, since the outlook is in many respects the same as ours. Then we want to thank Professor T. H. Berlin for many discussions and for his permission to use a few parts of a manuscript on which he and one of us (G. E. U.) have been working for quite some time.

G. E. UHLENBECK
G. W. FORD

CHAPTER I

The Explanation of the Laws of Thermodynamics

1. Introduction. In this chapter I will try to present an outline of the foundations of statistical mechanics, and I must apologize for the fact that it will not be a clear, axiomatic presentation. This is *not* because I am, as some physicists are, impatient with general discussions of fundamentals. On the contrary, I believe that further progress is intimately connected with a further clarification of the foundations. However, at present there is no generally accepted opinion of what the basic assumptions of the theory are, and as a result I can only present my own point of view, which is, I believe, a kind of paraphrase of the fundamental ideas of Boltzmann and Gibbs. And since these ideas were mainly developed in the attempt of explaining the laws of thermodynamics from the molecular theory of matter, I will follow also in this respect in the footsteps of the two founders of statistical mechanics.[1]*

First, let me remind you of the general problem of statistical physics. Given the structure and the laws of interaction of the molecules, what are the macroscopic properties of the matter composed of these molecules? To start one has therefore to say something about the molecular model and about the basic microscopic laws. For simplicity I will almost always assume:

(a) The motion of the molecules is governed by classical mechanics. It is true that the quantum mechanics adds new features to the problem; it may even be that the act of measurement introduces a "true" irreversibility into the theory as some authors claim. But most of the essential questions arise already in the classical theory, and since it is more familiar to you, I will restrict myself to this theory.

(b) The molecules are mass points interacting through central forces, which have the additivity property and which are of the van

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* Numbers refer to Notes at end of Chapter.

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der Waals or molecular type.   This means that the *given* Hamiltonian of the system of N particles is of the form:

$$(1) \qquad H = \sum_{i=1}^{N} \left[\frac{p_i^2}{2m} + U(\mathbf{r}_i) \right] + \sum_{i<j} \phi(|\mathbf{r}_i - \mathbf{r}_j|)$$

where the interaction potential $\phi(r)$ has the typical form shown in Fig. 1.   It consists of an attractive region with *finite range* r_1 and a
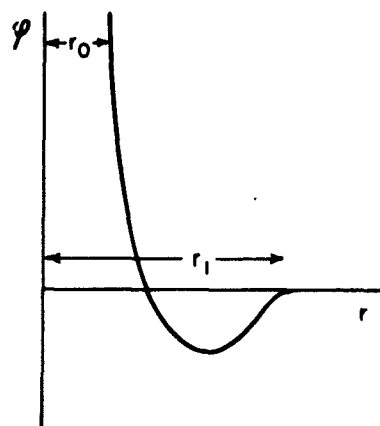
Figure 1

very steep repulsive part which can be taken as a *hard core* of radius r_0.[2]   In Eq. (1) $U(\mathbf{r}_i)$ is the potential of outside forces acting on the ith particle and includes the potential corresponding to the forces exerted by the walls of the container so as to keep the particles inside the volume V.   In fact this "wall potential" will usually be assumed to be the only outside force acting on the molecules.

The limited validity of these assumptions should be emphasized. The basic microscopic laws are surely quantum-mechanical, and the great richness of the macroscopic properties of matter can only be understood if more complicated molecular structures and other types of forces are taken into account.   Our assumptions would hold only, say, for gaseous or liquid Neon.   However, even with these simplifying assumptions there are still plenty of unsolved problems!   Also many of the questions, which we will consider, depend only on the qualitative features of the interactions and their treatment will therefore have a much wider validity.

2. The Liouville theorem. We represent the state of a mechanical system of n degrees of freedom by a point in the $2n$-dimensional phase space or Γ-space. In our case $n = 3N$, N = number of particles, and the coordinates of a point in Γ-space are $r_1 \cdots r_N$, $p_1 \cdots p_N$. In the course of time this Γ-point will move according to the Hamilton equations of motion:

(2)
$$\dot{q}_i = \frac{\partial H}{\partial p_i}, \qquad \dot{p}_i = -\frac{\partial H}{\partial q_i}, \quad i = 1, 2, \cdots, n.$$

Since these equations are of first order in the time it is clear that the path of the representative point in Γ-space will be determined by the initial point. To visualize the motion for all possible initial points, imagine that one has a very large number of copies of the system. Each copy sends a point in Γ-space, and if the number is large enough, one may consider the collection of points as a fluid streaming in Γ-space and possessing in any point a certain number density $\rho(q_1 \cdots q_n, p_1 \cdots p_n, t)$. The streamlines of the fluid motion are identical with the particle paths as determined by (2). With Gibbs we call this the *ensemble fluid* or just an *ensemble* of mechanical systems. One should note that the total number of copies never plays a role and is only introduced as an aid to visualize all the possible motions of the Γ-point. The ensemble fluid is a true continuum, and instead of the streaming of the fluid it may be better to speak of a continuous mapping of the Γ-space in itself. Soon also the density ρ will become the probability density that the system is in a region $dq_1 \cdots dp_n$ of Γ-space, and we shall then denote it by $D(q_1 \cdots p_n, t)$ and assume the normalization condition:

$$\int \cdots \int dq_1 \cdots dp_n \, D = 1.$$

In addition if the N particles are identical one should require that D be a *symmetric* function of the phases (r_i, p_i) of the separate particles.

A theorem which plays a central role is the theorem of Liouville,[3] which states that *the ensemble fluid moves as if it were an incompressible fluid*.

To prove this, note that the "velocity" V (components $\dot{q}_1 \cdots \dot{q}_n$, $\dot{p}_1 \cdots \dot{p}_n$) fulfills the condition:

(3)
$$\operatorname{div} V \equiv \sum_{i=1}^{n} \left(\frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i} \right) = \sum_{i=1}^{n} \left(\frac{\partial^2 H}{\partial q_i \partial p_i} - \frac{\partial^2 H}{\partial p_i \partial q_i} \right) = 0$$

by virtue of the Hamilton equations. Since one always has the continuity equation:

$$\frac{\partial \rho}{\partial t} + \text{div}\,(\rho \mathbf{V}) = 0$$

or:

$$(4) \qquad \frac{D\rho}{Dt} + \rho\,\text{div}\,\mathbf{V} = 0$$

with

$$(5) \qquad \frac{D}{Dt} \equiv \frac{\partial}{\partial t} + \mathbf{V}\cdot\text{grad}$$

$$\equiv \frac{\partial}{\partial t} + \sum_{i=1}^{n}\left(\dot{q}_i\frac{\partial}{\partial q_i} + \dot{p}_i\frac{\partial}{\partial p_i}\right)$$

it follows from (3) that:

$$(6) \qquad \frac{D\rho}{Dt} = 0$$

which means that ρ does not change if one moves with the fluid, or the fluid is incompressible.

If one stays at a fixed point in Γ-space then ρ changes according to:

$$\frac{\partial \rho}{\partial t} + \mathbf{V}\cdot\text{grad}\,\rho = 0$$

or:

$$(7) \qquad \frac{\partial \rho}{\partial t} = \sum_{i=1}^{n}\left(\frac{\partial H}{\partial q_i}\frac{\partial \rho}{\partial p_i} - \frac{\partial H}{\partial p_i}\frac{\partial \rho}{\partial q_i}\right) \equiv \{H, \rho\}$$

where $\{H, \rho\}$ is the Poisson bracket of H and ρ. This is the "Eulerian" way of expressing the incompressibility of the fluid. In the "Lagrangian" way of describing the motion of the fluid, the position $(q_1\cdots p_n)$ of a fluid element is given as a function of the initial position $(q_{10}\cdots p_{n0})$ and of the time. The condition for the incompressibility of the flow is now that the Jacobian:

$$(8) \qquad \frac{\partial(q_1\cdots p_n)}{\partial(q_{10}\cdots p_{n0})} = 1$$

which expresses the fact that if one follows a whole volume of points during the flow, this volume always stays the same, although of course

its shape will vary. Or in other words: the transformation of the Γ-space into itself induced by the flow preserves volumes. It is easy to see that the characterizations (7) and (8) are completely equivalent.

Two simple consequences of the Liouville theorem are worth noting:

(a) For any function $F(\rho)$ of the density, the integral:

$$\int \cdots \int F(\rho)\, dq_1 \cdots dp_n$$

taken over the whole Γ-space is independent of the time.

(b) Any density distribution ρ will be *stationary*, i.e. will not depend explicitly upon the time, if and only if ρ is constant along each streamline. In particular *any* distribution $\rho(H)$, which is a function of the Hamiltonian H, will be stationary, although such distributions are by no means the only stationary ones.

3. The approach to equilibrium; the ideas of Boltzmann. How can one "explain" the irreversible behaviour of macroscopic systems from the strictly reversible mechanical model? This question, which I call the problem of Boltzmann, has dominated the whole initial development of statistical mechanics and it is still being discussed. In its simplest form, one must "explain" in which sense an isolated (that is a conservative) mechanical system consisting of a very large number of molecules approaches thermal equilibrium, in which all "macroscopic" variables have reached steady values. This is sometimes called the *zeroth law of thermodynamics* and it expresses the most typical irreversible behaviour of macroscopic systems familiar from common observation.

The conflict with mechanics is most drastically shown if one recalls the famous *Poincaré recurrence theorem*. For a conservative system, the motion of the Γ-point will stay on the energy surface $H(q_1 \cdots p_n)$ $= E$. Furthermore the motion is *bounded* (in the momenta by the total energy E and the finite attractive potential energy; in the co-ordinates by the volume in which the molecules are enclosed). For such a mechanical system starting from a point P on the energy surface, the theorem says that for *any* region around P, there is a time T in which the phase point of the system will return to the region (see Fig. 2). Or in other words, the motion is quasi periodic, and there is apparently no trace of an approach to equilibrium. An outline of the proof of the Poincaré theorem is given in the notes.[4]

Let me now try to sketch the classical Boltzmann-Gibbs resolution

of this conflict. The general idea is that the two sides of the conflict refer to two different *levels* of observation or description of the system, namely the molecular and the macroscopic level. Clearly thermal equilibrium is a macroscopic notion. For its description it is *not* necessary to know the precise path of the Γ-point over the energy surface. It can be characterized by a small number (small compared to N) of "macroscopic" quantities. We shall see that it is due to this difference in description that one can understand and
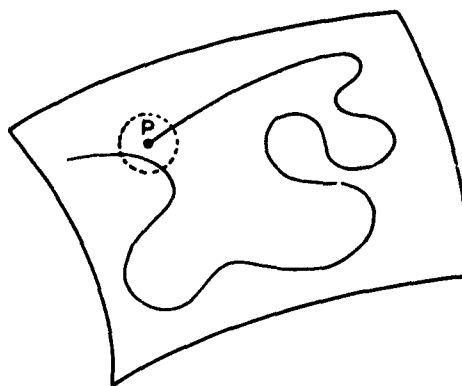
Figure 2

reconcile the apparently basic difference in the temporal behaviour on the two levels.

To see how this works, consider first with Boltzmann *the case of an ideal gas*. When the intermolecular forces can be neglected, then all macroscopic properties of the system are determined by the distribution of the N points representing the coordinates and momenta of the N molecules in the six dimensional phase space of a single molecule. We call this the μ-*space distribution*. To describe such a distribution of a *finite* number of points, one must divide the total μ-space (which is finite since it is limited by the volume of the vessel and the given total energy) in a large number M of small but finite regions or cells $\omega_1, \omega_2 \cdots \omega_M$, and one must record at a given time the numbers $n_1, n_2 \cdots n_M$ of points in these cells. The size of the cells must on the one hand be large enough so that the numbers n_i are appreciable and on the other hand small enough so that the n_i really give a presentation of the density distribution of the N points in μ-space. One sometimes expresses this compromise by saying that the cells must be

"physically infinitesimal". It is a compromise which *always* must be made in the description of an empirical distribution of a finite number of discrete entities.

Clearly the distribution $n_1, n_2 \cdots$ over the cells $\omega_1, \omega_2 \cdots$ in μ-space describes the state of the gas much less precisely than the description by one point in Γ-space. Each point in Γ-space corresponds to a definite distribution in μ-space, but the reverse is not true. In fact it is easy to prove that a given distribution in μ-space corresponds to a whole region ($6N$-dimensional) in Γ-space which has the volume:

$$(9) \qquad W = \frac{N!}{n_1! \, n_2! \, \cdots \, n_M!} \, \omega_1^{n_1} \omega_2^{n_2} \cdots \omega_M^{n_M}.$$

PROOF. Clearly the distribution n_i will not change if we move the molecules around in their cells. Moving, say, one of the molecules in the first cell around, leaving all other molecules fixed, will move the corresponding Γ-point over a six-dimensional volume ω_1. Since in Γ-space the states of the different molecules are represented by orthogonal six-dimensional sub-spaces, the motion of all N molecules in their cells will move the Γ-point over a "block" in Γ-space of the volume:

$$(10) \qquad \omega_1^{n_1} \omega_2^{n_2} \cdots \omega_M^{n_M}.$$

In addition the distribution n_i will not change if we permute two molecules in different cells and the motion of the molecules in their cells after the permutation will again produce a block of size (10) in Γ-space, which will have no common region with the previous block. Since there are:

$$(11) \qquad \frac{N!}{n_1! \, n_2! \, \cdots \, n_M!}$$

ways of dividing the N molecules in groups $n_1, n_2 \cdots$, the total volume in Γ-space will be given by the product of (10) and (11).

The set of numbers n_i is restricted by two subsidiary conditions:

$$(12) \qquad \begin{aligned} \sum_i n_i &= N, \\ \sum_i \varepsilon_i n_i &= E \end{aligned}$$

which express the conservation of total number and of total energy. Here ε_i denotes the energy of a particle in the cell ω_i. That one can assign this energy *independently* of the occupation numbers of the cells is clearly due to the assumption of the ideality of the gas. Note also that in (12) the value of E is not precisely determined, because the ε_i will vary slightly when the points move in their cells. The E in (12) is therefore not strictly the same as the given energy which determines the energy surface $H(q, p) = E$ in Γ-space on which the Γ-point moves. In fact the energy condition (12) determines two neighbouring energy surfaces around the given energy surface. The region in between we will call *the energy shell*; its thickness clearly depends again on the finiteness of the cells ω_i in μ-space.
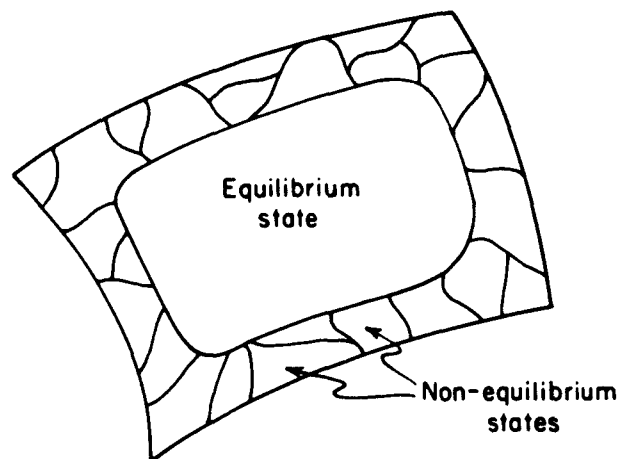
Figure 3

The volumes $W(n_1, n_2 \cdots)$ of the different distributions n_i over the cells ω_i in μ-space (as given by (9)) will cut out of the energy shell cylindrical regions of different size. Now one can prove the theorem:[5]

If N is very large then the so-called Maxwell-Boltzmann (M.B.) distribution:

$$(13) \qquad \bar{n}_i = A\omega_i e^{-\beta\varepsilon_i}$$

corresponds to a volume $\overline{W}$ which cuts out the overwhelmingly largest portion of the energy shell. In (13) the A and β are constants which must be determined from the subsidiary conditions (12). Schematically the division of the energy surface in Γ-space by the various

volumes $W(n_1, n_2 \cdots)$ is shown in Fig. 3. Boltzmann now identifies the M.B. distribution in μ-space with the thermal equilibrium state of the gas, and *all* other μ-space distributions with the macroscopic non-equilibrium states of the gas.

If we now *assume*, that in the motion of the Γ-point over the energy surface there is no preference for any portion of the surface and that in the course of time every accessible part of the surface will be reached, then it is very plausible that the time $t(A)$ during which the Γ-point is inside a region A is mainly determined by the magnitude of the area of A. Clearly one can then conclude:

1. If the gas is *not* in the thermal equilibrium state ($\equiv$ M.B. distribution), then it almost always will go into this state.

2. Once the gas is *in* the equilibrium state it will almost always stay there, although fluctuations away from equilibrium will and *must* occur because of the quasi-periodic character of the motion of the Γ-point.

This is the Boltzmann picture. It clearly reconciles the reversibility of the mechanical motion as expressed by the Poincaré theorem with the existence of a state of macroscopic equilibrium.

4. The generalization by Gibbs. The ergodic theorems. In the previous section we have avoided on purpose any mention of the word probability and of the ergodic hypothesis so as to emphasize the plausibility of the general ideas of Boltzmann. In order to generalize these ideas and to show the connection with the theory of probability and with the ergodic theorems, let us repeat the previous argument in a more abstract fashion.

Instead of describing the macroscopic state of the gas by the numbers $n_1, n_2 \cdots$ of points in the different cells of μ-space, one could also say that the macroscopic state of the gas is defined by the *values* of a number of macroscopic variables:

$$(14) \qquad y_i = f_i(x_1, x_2 \cdots x_N)$$

which are functions of the phases $x_k \equiv (\mathbf{r}_k, \mathbf{p}_k)$ of the N particles. For identical particles the functions f_i should of course be symmetric in the x_k. In fact in our case (ideal gas), one can take for these functions

$$(15) \qquad y_i = \sum_{k=1}^{N} \Delta_i(x_k), \quad i = 1, 2 \cdots M$$

where

$$\Delta_i(x) \begin{cases} = 1 & \text{if } x \text{ is in cell } \omega_i \text{ of } \mu\text{-space,} \\ = 0 & \text{otherwise.} \end{cases}$$

The values of the y_i are then clearly the numbers n_i in the cells ω_i, corresponding to the point $P \equiv (x_1 \cdots x_N)$ in Γ-space. Here again the question of the size of the cells ω_i comes up. Instead of saying that they should be physically infinitesimal, as explained in §3, so as to give the "best" description of the distribution in μ-space, one can also say that the sizes of the cells are essentially arbitrary and depend only on how detailed the macroscopic observation is. However, they always must be *finite*, so that corresponding to a given set of values of the y_i there is a *region* in Γ-space. In *addition* it must always be so that for one set of values of the macroscopic variables y_i, when N is very large, the corresponding region in Γ-space is overwhelmingly the largest. Of course in our case this follows as we saw from the explicit expression (9) for the volume of the Γ-space region.

In the general case, when the intermolecular forces are not neglected, it is clear that the μ-space distribution will not be enough to specify the macroscopic state of the system. For instance, often we will have to know how many pairs of molecules are in each other's action sphere since this will affect some of the macroscopic variables. However, we will still assume that the macroscopic state can be specified by giving the values of a number of phase functions y_i, so that

(a) each macroscopic state corresponds to a *region* in Γ-space and therefore to a portion of the energy shell, and so that:

(b) for large N there is one set of values of the y_i which corresponds to a region which is overwhelmingly the largest.[6]

For a given macroscopic description, that is for a given choice of the variables y_i, the energy shell will then be divided in *fixed* regions as indicated schematically in Fig. 3. Suppose now that at $t = 0$, one has "prepared" the system in a definite non-equilibrium macroscopic state. With this initial macroscopic state we associate an initial Γ-space probability distribution $D(P, t = 0)$ which is different from zero *only* in the corresponding region of the energy shell. Inside this region $D(P, 0)$ is in principle arbitrary, except that it should be a sufficiently smooth function of P. One can take for instance $D(P, 0)$ constant inside the region and zero otherwise. Note that we now write D for the density distribution ρ; D is normalized to unity.

This is *the only probability assumption* which one makes, and one can argue that it is the simplest assumption which is consistent with our macroscopic knowledge. From the Liouville equation one then can find in principle $D(P, t)$. It is the character of the change $D(P, 0) \to D(P, t)$ which determines everything. Gibbs in the notorious Chapter 12 of his book describes it about as follows. The

volume of the region where $D \neq 0$, remains according to Liouville the same, but the *shape* will change drastically.   Especially because of the sharp intermolecular forces two Γ-points which are originally close together will soon be far apart.   As a result the volume of the
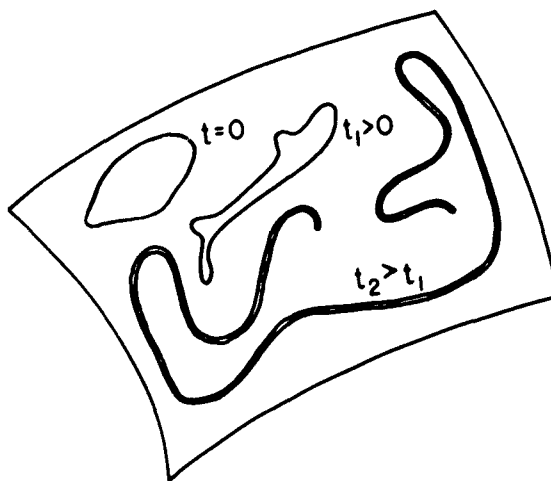
Figure 4

initial region will be drawn out to a very long and thin thread which more and more will wind through the whole energy shell (see Fig. 4; note that one should always think of the energy shell of points such that $E \leqq H \leqq E + \Delta E$, so that the thread is really a thin ribbon). One can expect therefore:

1. In the course of time the probability distribution D will become more and more uniform over the energy shell.   Of course this is meant *only* in the coarse-grained sense; the distribution will always consist of a thin filament more or less uniformly wound through the energy shell.   The distribution which is uniform within the energy shell we will call with Gibbs *the microcanonical ensemble.* .

2. This approach to uniformity will continue when t increases, *although* each Γ-point will move quasi-periodically according to the Poincaré theorem.

3. The time it takes until uniformity is reached will depend *essentially* on how one judges the uniformity, that is to say on the size of the finite regions in which the energy shell is divided according to the chosen macroscopic description.

4. For any macroscopic description there comes a time when the probability of each macroscopic state is determined by the size of the corresponding region of the energy shell. Since for large N, there is one region which is overwhelmingly the largest this will then also be the most probable state and it characterizes the thermal equilibrium of the system.

I hope I have made clear the similarity between the Boltzmann picture and the more general argument of Gibbs. Of course in both cases a number of statements were made without proof, and they may seem so vague that they are not amenable to proof! It is therefore of great interest that at least part of the argument can be formulated much more precisely by means of the Birkhoff ergodic theorems.[7] Let me remind you of these theorems:

(a) For a bounded mechanical motion and for any phase function $y = f(P)$ which is integrable over the energy surface, the *time average*:

$$(16) \qquad \bar{y} = \lim_{T \to \infty} \frac{1}{T} \int_0^T dt\, f(P_t)$$

almost always exists. Here P_t denotes the phase point which evolves from the initial point P_0 by the motion. Furthermore $\bar{y}$ is independent of the choice of the initial point on the trajectory, but $\bar{y}$ can vary with the trajectory.

I will not try to indicate the proof since it is quite tricky. All that is used is the boundedness of the motion and the Liouville theorem. It is therefore certainly applicable to the Gibbs macroscopic variables y_i.

(b) For a *metrically transitive* system the time average (16) is independent of the trajectory chosen and is equal to the *ensemble average*

$$(17) \qquad y_\nu = \int \cdots \int d\Omega\, f(P)\sigma(H).$$

Here the integral goes over the energy surface and $\sigma(H)$ is the distribution over the energy surface which corresponds to the uniform distribution in the energy shell, so that:

$$(18) \qquad \sigma(H) = \frac{\text{const.}}{|\text{grad } H|}$$

where the constant is to be determined by the normalization condition:

$$\int \cdots \int \sigma(H)\, d\Omega = 1.$$

$\sigma(H)$ is called the microcanonical surface distribution.

A mechanical system is metrically transitive if the energy surface can *not* be divided into two finite regions such that the orbits starting from points in one of the regions always remain in that region. It is clearly a more precise formulation of the idea that in course of time the path of the Γ-point will fill the whole energy surface which we used in the Boltzmann-Gibbs argument.[8] Of course it is very difficult (and it has not been achieved) to prove for a given Hamiltonian that the motion is or is not metrically transitive, and even examples which can be discussed exactly are rare.[9] However, the advantage of a precise formulation remains. Note still that in principle it is *not* necessary for the equality of the time and phase averages that the mechanical system has a large number of degrees of freedom, although it seems more likely that the system will be metrically transitive if N is large.

Let us now return to the Boltzmann-Gibbs picture of the approach to equilibrium. First, by taking in (16) and (17) for $f(P)$ the characteristic function of a region A on the energy surface (that is $f(P) = 1$ if P is inside A and $f(P) = 0$ otherwise), it follows that for a metrically transitive system:

$$(19) \qquad \lim_{T \to \infty} \frac{t(A)}{T} = \frac{V(A)}{V}$$

where t is the time the phase point spends in A, and where $V(A)$ is the volume of the part of the energy shell, whose total volume is V, which is based on A. This is clearly the precise formulation of the assumption essential for the Boltzmann picture that the time $t(A)$ is mainly determined by the magnitude of the area of A.[10]

Also the argument of Gibbs can now be expressed more precisely. The assumption that for large N there is one set of values of the macroscopic variables y_i which correspond to by far the largest part of the energy surface, can be replaced by the requirement that the variables y_i must be *normal variables*.[11] By this we mean that for large N the y_i must have the property:

$$(20) \qquad \{ \langle y_i^2 \rangle - \langle y_i \rangle^2 \}^{1/2} \ll \langle y_i \rangle$$

or in words: the fluctuation of each of the y_i must be very small compared to $\langle y_i \rangle$ itself. Here the average values are always taken as in (17) over the microcanonical ensemble. It is then clear that if

one starts at $t = 0$ with the initial distribution $D(P, 0)$ the *expectation* values of the variables y_i defined by:

$$(21) \qquad \bar{y}_i(t) = \int \cdots \int d\Omega\, f_i(P) D(P, t)$$

will start with the values $y_i(0)$ corresponding to $D(P, 0)$ and become for $t \rightarrow \infty$ the $\bar{y}_i(\infty) = \langle y_i \rangle$ which for a large system are very closely equal to the equilibrium values.[12] This is so, because from the ergodic theorems and from (20) one can conclude that for almost all trajectories and for the overwhelmingly largest *time* the y_i must have constant values. Note still that with the "Boltzmann" y_i as given by (15) the $\bar{y}_i$ are the expectation values of the numbers n_i in the cells ω_i at time t.[*] These are connected with the so-called *first distribution function* $F_1(x_1, t)$ defined by:

$$(22) \qquad \frac{1}{V} F_1(x_1, t) = \int \cdots \int dx_2 \cdots dx_N\, D(x_1 \cdots x_N, t).$$

In fact if one smoothes the $\bar{n}_i(t)$ over the cells then the "histogram" becomes a smooth function $f(x, t)dx$ where:

$$f(x, t) = \int \cdots \int dx_1 \cdots dx_N \sum_{i=1}^{N} \delta(x - x_i) D(x_1 \cdots x_N, t)$$

$$= \frac{N}{V} F_1(x, t).$$

Similarly to (22) one can define the second or pair distribution function and in general the s-tuple distribution function by:

$$(23) \qquad F_s(x_1, \cdots x_s, t) = V^s \int \cdots \int dx_{s+1} \cdots dx_N\, D(x_1 \cdots x_N, t).$$

We will come back to these functions in Chapter VII.

Let me conclude this section with some remarks about the bothersome notion of the macroscopic variables or of the macroscopic "observer", since it has led to so much controversy.

1. The notion of macroscopic variable may seem a bit vague, but this cannot be helped as long as the discussion is kept in general terms.

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[*] Note that in §3 the $\bar{n}_i$ denoted the *maximizing* set of values of the n_i, which are the equilibrium values. For large N they are closely equal to what is here denoted by $\bar{n}_i(\infty)$ or by $\langle n_i \rangle$.

In Chapter VII we shall see that the expectation values of the usual macroscopic variables (as stress tensor, temperature distribution, etc.) can be found from the first few of the distribution functions (23).

2. There is an element of arbitrariness in the concept of the macroscopic description of the system, which may seem objectionable. However, it is clear that in principle the macroscopic knowledge of the state of the system depends so to say on the zeal of the observer and can therefore not be defined in general. All one *can* say is that the macroscopic description is a *contracted* description, which uses much fewer variables than required for the precise microscopic specification. Also, in practice, it usually is clear what the macroscopic variables are, since they are dictated by the experimental phenomena which one tries to explain. To avoid the arbitrariness by introducing the concept of a probability distribution over all possible macroscopic observers,[13] as some authors have done, seems to me only to increase the confusion.

3. The arbitrariness of the macroscopic description affects the time required for the expectation values $\bar{y}_i(t)$ to reach their equilibrium values $\langle y_i \rangle$, since the choice of the y_i determines the size of the regions in which the energy shell is divided. One expresses this often by saying that the relaxation to equilibrium depends on the coarse graining. I think this is surely the case, but on the other hand it is clear that the relaxation to equilibrium will *also* depend on the Hamiltonian, that is on the structure of the mechanical system, and it is *this* dependence in which one is usually more interested, since the choice of the y_i is fixed by the experimental situation.

4. The variation in time of the $y_i(t)$ in principle will always depend on the initial probability distribution $D(P, 0)$ in Γ-space. This again seems objectionable, because of the arbitrariness. Even if one says that $D(P, 0)$ should be chosen so as to correspond with our initial macroscopic knowledge of the system, it is clear that this cannot possibly determine $D(P, 0)$ completely. The answer is, I think, that one is only interested in that part of the relaxation of the y_i to equilibrium which is *independent of the choice of* $D(P, 0)$. One should expect that in a proper macroscopic experiment this will be the case after a short "*chaotization period*". Or one can say that after such a short period the temporal development of the y_i will be determined by the y_i themselves through equations which are of the first order in time. I call this *the requirement of macroscopic causality*. It is a condition on the choice of the macroscopic description, which clearly

can only be fulfilled in some asymptotic sense. We will come back to this in Chapter VII.

5. The laws of thermodynamics. We must now discuss the connection with or the "explanation" of the laws of thermodynamics. In the usual formulation of these laws, this means that we have to explain the following five basic facts and notions.

(a) *The existence of thermodynamic equilibrium for a closed system.* This is the so-called zeroth law referred to in §3.[14] Let me assume that it was sufficiently elucidated in the previous sections!

(b) *The notion of temperature.* In thermodynamics the equilibrium is in the first place characterized by the temperature. In order to represent the temperature by a number one must show besides the existence of an equilibrium state, that the equilibrium state has the *transitive property*. If system A is in equilibrium with the systems B and C separately then B and C are also in equilibrium between themselves. Here we mean by equilibrium of two systems the fact that the macroscopic properties of the systems will not change when the systems are coupled "weakly" together. The coupling must allow interchange of energy between the systems, but the interaction energy must be completely negligible compared to the energy of each of the two systems.

(c) *The first law of thermodynamics.* Since the molecular model is always taken to be a conservative mechanical system, so that the total energy is already conserved, the only question which remains is that of the distinction between the notions of quantity of heat and of external work.

(d) *The second law of thermodynamics for reversible phenomena.* Knowing how the temperature T and the quantity of heat Q have to be interpreted, one must show that for a "reversible" change of the macroscopic state $\delta Q/T$ is a perfect differential of a function (the entropy) of the macroscopic state of the system.

(e) *The second law of thermodynamics for irreversible phenomena.* This says that in an irreversible or spontaneous change from one equilibrium state to another (as for example the equalization of temperature of two bodies A and B, when brought in contact) the entropy always increases.

In the following we will discuss these points in succession.

6. The notion of temperature. The canonical ensemble. For the introduction of the notion of temperature we have to discuss the equilibrium of the system A under consideration when it is weakly

coupled to a very large "heat reservoir" B. Under weakly coupled we mean that the total Hamiltonian can still be taken as:

$$(24) \qquad H = H_A + H_B$$

although A and B interact and can exchange energy. We assume that the total system $A + B$ is in equilibrium in the sense of the micro-canonical ensemble. The question is now to find the probability that the system A is in a certain element $d\Gamma_A$ of its phase space. We will *prove* that in the limit that system B is very large, this probability is:

$$(25) \qquad D_A \, d\Gamma_A = C e^{-\beta H_A} \, d\Gamma_A$$

where the constant C is determined by the normalization and where β is a parameter which depends on the system B but in the limit is independent of its size. The probability distribution (25) Gibbs calls the *canonical ensemble*.

There are many versions of the proof of this theorem[15] and it can be presented in various degrees of rigour. The following simple proof fulfills I think all the physical requirements. Let $V(E)$ be the volume in Γ-space of the region where $H \leq E$, and call $S(E) = dV/dE$. $S(E)$ is then the "area" of the energy surface $H = E$, which can also be expressed as:

$$S(E) = \int \cdots \int_{H \, E} \frac{d\Omega}{|\text{grad } H|}.$$

The micro-canonical distribution in Γ-space can now be written in the form:

$$(26) \qquad D_{\text{micro can.}}(x_1 \cdots x_N) \, d\Gamma = \frac{\delta(H - E)}{S(E)} \, d\Gamma$$

using the Dirac δ-function. If the two systems A and B are in equilibrium in the sense of the micro-canonical ensemble with the *total* energy E, then, since the two Γ-spaces are orthogonal to each other, one has for the distribution in the combined Γ-space:

$$(27) \qquad D \, d\Gamma_A \, d\Gamma_B = \frac{1}{S(E)} \, \delta(H_A + H_B - E) \, d\Gamma_A \, d\Gamma_B$$

where:

$$(28) \qquad S(E) = \int_0^E d\varepsilon \, S_A(\varepsilon) S_B(E - \varepsilon)$$

as follows immediately from the normalization. The distribution function for system A irrespective of the state of B is therefore:

$$
\begin{aligned}
(29) \qquad D_A \, d\Gamma_A &= \frac{d\Gamma_A}{S(E)} \int d\Gamma_B \, \delta(H_A + H_B - E) \\
&= \frac{d\Gamma_A}{S(E)} \int dE_B \, S_B(E_B) \, \delta(H_A + H_B - E) \\
&= \frac{S_B(E - H_A)}{S(E)} \, d\Gamma_A.
\end{aligned}
$$

In most proofs, to make things definite, one assumes that B consists of a large number of weakly coupled systems, so that in turn

$$H_B = H_1 + H_2 + \cdots + H_N.$$

Physically this means that one assumes the heat reservoir B to be an ideal gas, and there is clearly nothing against that. But then we may as well assume that B is an ideal gas of N point molecules, in which case:

$$H_B = \sum_{i=1}^{N} \frac{p_i^2}{2m}.$$

The energy surface then becomes a hypersphere of radius $(2mE)^{1/2}$ in the $3N$ momentum directions and a hypercube of edge L ($V = L^3 =$ volume of the vessel) in the $3N$ coordinate directions, so that clearly:

$$(30) \qquad S_B(E) = C_N E^{(3N-1)/2}$$

indicating only the dependence on E. Now write (29), using (28) in the form:

$$D_A \, d\Gamma_A = d\Gamma_A \frac{S_B(E - H_A)}{S_B(E)} \bigg/ \int_0^E d\varepsilon \, S_A(\varepsilon) \frac{S_B(E - \varepsilon)}{S_B(E)}.$$

From (30) and for large N:

$$(31) \qquad \frac{S_B(E - \varepsilon)}{S_B(E)} = \left(\frac{E - \varepsilon}{E}\right)^{(3N-1)/2} \cdots > e^{-\beta\varepsilon}$$

with:

$$(32) \qquad \beta = \frac{d \ln S_B}{dE} \simeq \frac{3N}{2E}$$

in which all that is assumed is that we are interested only in values of $\varepsilon \ll E$. Since D_A is constant on energy surfaces $H_A = \varepsilon$ one gets:

$$(33) \qquad D_A \, d\Gamma_A = d\Gamma_A \, \frac{e^{-\beta H_A}}{\int_0^\infty d\varepsilon \, S_A(\varepsilon) e^{-\beta \varepsilon}}$$

which is of the form (25) and which is automatically normalized to one, since:

$$\int \cdots \int d\Gamma_A \, D_A(H) = \int_0^\infty d\varepsilon \, S_A(\varepsilon) D_A(\varepsilon).$$

Note that $1/\beta$ is proportional to the average energy per particle of the heat reservoir and is in this sense independent of the "size" of the reservoir.

Note that if we had several systems $A_1, A_2 \cdots$ each coupled to the very large reservoir B, then the probability for each of them to be in their region $d\Gamma_{A_i}$ is given by the canonical distribution *with the same* β. The quantity β has therefore all the required temperature properties and it must be an universal function of the thermodynamic temperature.

Note, finally, that the system A will always be canonically distributed, whatever its size. It could consist of a few or even one molecule. However, we will only use the theorem in the case that A is of macroscopic size. In this case because of the steepness of increase of $S_A(E)$ with E, the canonical distribution (33) will be very narrow around the average value, so that then the difference between the canonical and the micro-canonical distribution will be slight.[16]

7. The first law of thermodynamics. Since both in the first and in the second law of thermodynamics one considers changes of the macroscopic state of the system, we first need to look more closely at the outside potential U in the Hamiltonian (1) through which the changes of state are produced. In general one can say that this potential $U(r_i, a_1, a_2 \cdots)$ will depend, besides on the position r_i of the ith molecule, on a number of parameters a_k which characterize the outside fields. Suppose for instance that the outside field is produced by m fixed and independent centres of force. Then:

$$U(\mathbf{r}_i, a_1, a_2 \cdots) = \sum_{k=1}^{m} \Phi_k(|\mathbf{r}_i - \mathbf{R}_k|)$$

and the parameters a_k are the positional coordinates $\mathbf{R}_k$ of the centres.

The force on the ith molecule:

$$(34) \qquad \mathbf{F}_i = -\left(\frac{\partial U}{\partial \mathbf{r}_i}\right)_{\mathbf{R}_k \text{ fixed}}$$

is equal and opposite to the sum of the forces:

$$(35) \qquad \sum_{k=1}^{m} \mathbf{X}_k = -\sum_{k=1}^{m} \left(\frac{\partial \Phi_k}{\partial \mathbf{R}_k}\right)_{\mathbf{r}_i \text{ const.}}$$

exerted by the ith molecule on the centres as required by Newton's third law.

Although it is always possible to describe the outside force fields in such detail that the equality of action and reaction is put in evidence, it is in general *not* convenient to do so. Already if the force centres R_k are *not* independent but are rigidly connected to each other, then it is clearly indicated to describe the centres by the six coordinates of the rigid structure of connected sources. In this case the force F_i on the ith molecule is still related to the generalized force:

$$(36) \qquad X_k = -\left(\frac{\partial U}{\partial a_k}\right)_{\mathbf{r}_i \text{ const.}}$$

acting "in the direction a_k" on the sources, but the relation is more complicated than in (34) and (35). In the general case we will therefore not bother with the relation between the force:

$$\mathbf{F}_i = -\left(\frac{\partial U}{\partial \mathbf{r}_i}\right)_{a_k \text{ const.}}$$

acting on the ith molecule and the generalized force X_k in the direction a_k. The forces X_k will determine the work done *on* the gas for *fixed* configuration of the molecules if one changes the outside force fields by changing the parameters a_k. In fact this work will be given by:

$$(37) \qquad \delta W = -X_1 \, \delta a_1 - X_2 \, \delta a_2 - \cdots$$

where the equality of action and reaction is used implicitly.

Turning now to the first law of thermodynamics, I have remarked already that since conservation of energy is so to say built into the theory the only question remaining is how to distinguish between the external work W done on the system and the quantity of heat Q put into the system.

Work can only be done on the gas by changing the parameters a_k, and from (36) and (37) we see that the work done on the gas is:

$$(38) \qquad \delta W = -\sum_k X_k \, \delta a_k$$

where:

$$(39) \qquad \bar{X}_k = \int \cdots \int d\Gamma \left(- \frac{\partial H}{\partial a_k} \right) D$$

is the force in "direction" a_k averaged over all the configurations of the gas. If one takes for D the microcanonical distribution then clearly δW must be equal to the increase δE of the energy, or in thermodynamical language the change δ is then an adiabatic one. If, however, one takes for D the *canonical* distribution, then after the change δa_k of the parameters a_k the original distribution will in general not be an equilibrium distribution with respect to the heat reservoir. A redistribution will take place, which will change the average energy, and we will *define* the quantity of heat δQ put *into* the system by:

$$(40) \qquad \delta Q = \delta \bar{E} - \delta W.$$

That this is appropriate can be seen also by saying that the average energy can also be changed by changing the β of the heat reservoir without changing the parameters a_k, and in this case the change should clearly be called the heat put into the system.

Note finally that since usually the *only* outside potential we consider is the wall potential for which there is only one parameter a_k namely the volume V of the vessel, one can write in this case Eq. (38)

$$W = - p\, \delta V$$

where:

$$(41) \qquad p = \int \cdots \int d\Gamma \left(- \frac{\partial H}{\partial V} \right) D$$

is clearly the pressure exerted by the gas which if D is the canonical ensemble will be a function of V and β. The macroscopic state of the system is then specified by V and β, or in the general case by β and the parameters a_k.

8. The second law of thermodynamics. We will now show that for a change δ in which *both* the β of the heat reservoir *and* the parameters a_k are changed in such a slow or "reversible" way that the system may always be considered to be canonically distributed, the quantity $\beta \delta Q$ is a perfect differential of a function of the state of the system, that is a function of β and the a_k.

To prove this, write the average energy in the form:

$$\bar{E} = \frac{\int d\Gamma\, H e^{-\beta H}}{\int d\Gamma\, e^{-\beta H}} = - \frac{\partial}{\partial \beta} \ln Z$$

with:

(42)
$$Z = \int d\Gamma \, e^{-\beta H}.$$

Hence:

$$\delta E = -\frac{\partial^2}{\partial\beta^2}(\ln Z)\,\delta\beta - \sum_k \frac{\partial^2}{\partial\beta\partial a_k}(\ln Z)\,\delta a_k.$$

From (38) follows that the work done on the system can be written as:

$$\delta W = \frac{\int d\Gamma \, e^{-\beta H} \sum_k \frac{\partial H}{\partial a_k}\,\delta a_k}{\int d\Gamma \, e^{-\beta H}} = -\frac{1}{\beta}\sum_k \frac{\partial \ln Z}{\partial a_k}\,\delta a_k.$$

Therefore:

$$\beta\,\delta Q = \beta(\delta E - \delta W)$$

(43)
$$= -\beta \frac{\partial^2 \ln Z}{\partial\beta^2}\,\delta\beta - \sum_k \left[\beta \frac{\partial^2 \ln Z}{\partial\beta\,\partial a_k} - \frac{\partial \ln Z}{\partial a_k}\right]\delta a_k$$

$$= -\frac{\partial}{\partial\beta}\left[\beta\frac{\partial \ln Z}{\partial\beta} - \ln Z\right]\delta\beta - \sum_k \frac{\partial}{\partial a_k}\left[\beta\frac{\partial \ln Z}{\partial\beta} - \ln Z\right]\delta a_k$$

$$= \delta\left[\ln Z - \beta\frac{\partial \ln Z}{\partial\beta}\right] = \delta\left[-\beta^2 \frac{\partial}{\partial\beta}\left(\frac{1}{\beta}\ln Z\right)\right]$$

which concludes the proof.

Comparison with $\delta Q/T = \delta S$ shows that:

(44)
$$\beta = \frac{1}{kT}$$

$$S = -k\beta^2 \frac{\partial}{\partial\beta}\left(\frac{1}{\beta}\ln Z\right) + \text{const.}$$

(45)
$$= \frac{\partial}{\partial T}(kT \ln Z) + \text{const.}$$

where T is the absolute thermodynamic temperature, S the entropy and k an universal constant which cannot be determined from this argument. To find k, one must consider the case of an ideal gas, enclosed in the volume V. Then:

$$Z = \int_V \cdots \int_V d\mathbf{r}_1 \cdots d\mathbf{r}_N \int \cdots \int d\mathbf{p}_1 \cdots d\mathbf{p}_N \exp\left(-\beta \sum_i \frac{p_i^2}{2m}\right)$$

$$= V^N (2\pi m kT)^{3N/2}.$$

From (41) this gives for the pressure:

$$(46) \qquad p = \frac{\partial}{\partial V}(kT \ln Z) = \frac{NkT}{V}.$$

So one gets the ideal gas law if $k = R/N$ is the gas constant per molecule.

I will omit a more detailed discussion about the question in which precise sense the entropy S as defined by (45) has also the property (required by the second law for irreversible processes) of increasing in any spontaneous transition from one equilibrium state to another. Since we have explained the zeroth law the reader will believe that this part of the second law, which is a more precise expression of the irreversible behaviour of macroscopic systems, can be "explained" in a similar way.

Finally a remark about the constant in the equation (45) for the entropy. Clearly from the argument given it is *not* possible to fix this constant and one cannot even determine its dependence on the number of particles N. Thermodynamically only entropy differences between states which can be connected by a reversible transition are operationally defined. Therefore since N is fixed, the dependence of the entropy on N can only be agreed upon by *convention*.[17] However, it certainly is a sensible convention to require that the entropy at fixed T and for large N and large V, so that $v = V/N$ is fixed, becomes of the form:

$$(47) \qquad S = N\eta(v, T).$$

The entropy becomes then a so-called *extensive variable*, that is proportional to the size of the system when the *intensive variables* T and v are given. In addition one also would like to insure that all the classical results agree in the limit $T \to \infty$ with the results of the quantum statistics, if one makes the usual assumption that each non-degenerate energy level has the statistical weight equal to one. Note that this is of course also a *convention*, since only the ratios of the weights of different levels have operational meaning, but it certainly is a very appealing convention. *Both* these objectives are realized by omitting the constant in (45) and by defining Z instead of by (42), by:

$$(48) \qquad \begin{aligned} Z(V, T, N) &= \frac{1}{N!h^{3N}} \int d\Gamma \, e^{-\beta H} \\ &= \frac{1}{N!\lambda^{3N}} \int_V \cdots \int_V d\mathbf{r}_1 \cdots d\mathbf{r}_N \exp\left(-\frac{1}{kT}\sum_{i<j}\phi(r_{ij})\right) \end{aligned}$$

where h is Planck's constant, $\lambda = h/(2\pi mkT)^{1/2}$, and where in the second line the integration over the momenta has been carried out. Z is called *the partition function*. Comparison with the thermodynamic formulas then shows that:

$$(49) \qquad \qquad \Psi(V, T, N) = -kT \ln Z$$

is the (Helmholtz) free energy, from which all other macroscopic quantities follow.   Especially:

$$(50) \qquad \begin{aligned} S &= -\frac{\partial \Psi}{\partial T}, \qquad && p = -\frac{\partial \Psi}{\partial V}, \\[2mm] \bar{E} &= \Psi - T\frac{\partial \Psi}{\partial T}, \qquad && C_v = \left(\frac{\partial \bar{E}}{\partial T}\right)_v = -T^2\frac{\partial^2 \Psi}{\partial T^2} \end{aligned}$$

and so on.   In Chapter II we will show that for large N and V, $v = V/N$ fixed:

$$(51) \qquad \qquad \Psi(V, T, N) = N\psi(v, T)$$

from which (47) follows.

NOTES ON CHAPTER I

1. For a critical discussion of the foundations of statistical mechanics the article of P. and T. Ehrenfest (*Begriffliche Grundlagen der Statistischen Auffassung in der Mechanik*, Enzyclopädie der Math. Wiss. Vol. IV, Art. 32, 1912), is still indispensable. It is now also available in English translation (by M. J. Moravcsik, Cornell University Press, 1959). For a recent account and for the recent literature see for instance A. Münster, *Prinzipien der Statistischen Mechanik*, Handbuch der Physik, Vol. III/2, 1959.

The difference in attitude with respect to the foundations is for instance illustrated by the fact that a mathematician (e.g. Khinchin, see his book: *Mathematical Foundations of Statistical Mechanics*, translated by G. Gamov, Dover reprint, 1949), is inclined to look upon the ergodic theorems of Birkhoff e.o. as the proper basis for the theory, while a physicist is often inclined to think that these theorems are either almost obvious or not really essential. This is for instance the view expressed by Landau and Lifshitz in their excellent book *Statistical Physics* (Pergamon Press, London, 1958). These authors start from the beginning *not* with a closed system, but with a system interacting with a large heat reservoir. Other physicists (e.g. Tolman in his well known book, *The Principles of Statistical Mechanics* (Oxford, 1938)) more or less postulate the microcanonical ensemble as the representation of a closed system in thermal equilibrium. It is true that in either of these two ways one can avoid the vexing problem of the approach to equilibrium while one keeps all that is needed for the treatment of the problems of the equilibrium theory. However, it seems to us that the goal should be an unified treatment of *both* equilibrium and non-equilibrium statistical mechanics. To do this, one cannot avoid the ergodic problem, and the Birkhoff ergodic theorems then become an important first step, which however does *not* exhaust the subject!

2. The assumptions of a hard core and of a finite range are only made in order to have a definite mathematical model for the inter-molecular potential. From the quantum theory of the van der Waals' forces between neutral molecules it only follows that at short distances one has a very sharp repulsion while at larger distances

there is an attraction which goes to zero as $1/r^6$.   Since the theory does not give an explicit expression for $\phi(r)$ it is customary to use simple semi-empirical formulas, as for instance the so-called Lennard-Jones (12, 6) potential:

(a)
$$\phi(r) = 4\varepsilon \left\{ \frac{1}{(r/\sigma)^{12}} - \frac{1}{(r/\sigma)^6} \right\}$$

which represents the two features of $\phi(r)$ which the quantum theory predicts.   We will come back to this in Chapter II.

3. The theorem of Liouville proves that the volume in phase-space is a so-called *integral invariant* of the motion.   It is well known that the volume is only one of a series of such integral invariants which were discovered by Poincaré.   One can prove that for any ensemble flow and for any s such that $1 \leq s \leq n$:

(b)
$$\frac{D}{Dt} \int \cdots \int_{(2s)} \sum_{i_1 \cdots i_s} dq_{i_1}\, dp_{i_1}\, dq_{i_2}\, dp_{i_2} \cdots dq_{i_s} dp_{i_s} = 0.$$

In here the integral goes over a $2s$-dimensional surface and the sum goes over all $_nC_s$ different combinations of the indices $i_1 \cdots i_s$.   Eq. (b) states that the integral does not change if one moves with the fluid. For $s = n$ Eq. (b) becomes the Liouville theorem in the Lagrangian form.   Compare E. T. Whittaker, *Analytical Dynamics*, 4th ed. (Cambridge University Press, Cambridge, 1960), Chapter 10, or for a more succinct discussion H. Goldstein, *Classical Mechanics* (Addison-Wesley Press, Cambridge, Massachusetts, 1950), pp. 247–250.

One might well ask the reason why the particular case of (b) represented by the Liouville theorem plays such a special role in statistical mechanics.   We think the simple answer is that the Liouville theorem is the only invariance theorem which affects the change of the density ρ.   Only for singular density distributions, in which the members of the ensemble would be distributed over surfaces of dimensionality less than $2n$, would the more general invariance properties (b) be of importance.

4. Proof of the Poincaré recurrence theorem.   We follow the presentation by M. Kac in the Boulder lectures of 1957 (*Probability and related topics in physical sciences*, p. 63).   Let A be the region on the energysurface $H = E$ around the initial point P (see Fig. 2).   If we follow all the points of A in their motion, then it is easy to show that:

(c)
$$\mu(A) = \int \cdots \int_A \frac{d\Omega}{|\operatorname{grad} H|}$$

remains the same.   To see this, consider two energysurfaces $H = E$ and $H = E + \Delta E$.   If Δn is the normal distance between these two surfaces, then according to Liouville the cylindrical volume:

$$\int \cdots \int d\Omega\, \Delta n$$

will be conserved.   Since $\Delta E = |\text{grad } H|\Delta n$ and ΔE is fixed this implies that (c) remains constant.   Call $\mu(A)$ the measure of the region A.   This is therefore a positive and finite number associated with A which is conserved in the streaming over the energysurface.   Since the total area of the energysurface is finite because of the boundedness of the motion also the total measure of the energysurface will be finite.

Suppose now that there are points in A which in their motion would *never* come back to A and that there are so many of such points that they would fill a subregion B in A, which has a *finite* measure.   We will prove that this is *impossible*.   Follow namely the region B in its motion and consider the corresponding regions $B_1, B_2, \cdots$ occupied by the points of B at the later times $\Delta, 2\Delta \cdots$.   If Δ is chosen large enough so that B and B_1 do not overlap it follows that *none* of the regions $B, B_1, B_2, \cdots$ overlap.   To see this note that if say B_n and B_{n+k} had points in common, then from the unicity of the motion (the impossibility of the crossing of two streamlines) it follows by tracing the motion backwards that also B_{n-1} and B_{n+k-1} must have points in common.   Continuing this argument one would end up with the statement that B itself must have points in common with B_k, which means that B contains points which after the time $k\Delta$ would have returned to A.   But this is contrary to the supposition that B is a region containing all points which never come back.   If the regions $B, B_1, B_2, \cdots$ do not overlap, then since $\mu(B) = \mu(B_1) = \mu(B_2) = \cdots$ the total measure of all these regions would be infinite, which is impossible since the measure of the total energysurface is finite.   Hence one concludes that the measure of all points in A, which will never return to A must be zero, which is the Poincaré theorem.

5. The proof can be given with various degrees of precision.   The simplest way, following Boltzmann and Tolman (*Principles of Statistical Mechanics*, p. 79) is to take the logarithm of W and to apply the Stirling approximation in the weak form:

(d) $\qquad\qquad\qquad \log n! = n \log n - n.$

One then gets:

(e) $\qquad\qquad \log W = N \log N - \sum_i n_i \log n_i + \sum_i n_i \log \omega_i.$

Varying the n_i by Δn_i, one obtains:

(f) $\log \dfrac{W + \Delta W}{W} = \sum_i \Delta n_i(-\log n_i - 1 + \log \omega_i) - \dfrac{1}{2} \sum_i n_i \left(\dfrac{\Delta n_i}{n_i}\right)^2 + \cdots$.

The Δn_i have to fulfill the subsidiary conditions:

$$\sum_i \Delta n_i = 0, \qquad \sum_i \varepsilon_i \Delta n_i = 0$$

because N and E are given.   Multiplying these conditions with the Lagrange multipliers ($\log A + 1$) and ($-\beta$) respectively, and adding the result to (f), one sees that the first variation vanishes for the set fulfilling the conditions:

$$-\log \bar{n}_i + \log A + \log \omega_i - \beta \varepsilon_i = 0$$

or:

$$\bar{n}_i = A \omega_i e^{-\beta \varepsilon_i}.$$

That for this set W is a very sharp maximum follows from (f) since for this set:

(g) $\log \dfrac{\overline{W} + \Delta W}{\overline{W}} = -\dfrac{1}{2} \sum_i \bar{n}_i \left(\dfrac{\Delta n_i}{\bar{n}_i}\right)^2 \cong -N\langle(\Delta n_i/\bar{n}_i)^2\rangle \mathrm{av}$

if $\overline{W}$ is the value of W for $n_i = \bar{n}_i$.   Clearly if N is very large then even a very small average relative deviation $\langle \Delta n_i/\bar{n}_i\rangle$ from the $\bar{n}_i$ will reduce the corresponding volume enormously.

From this proof we see that a more correct statement of the theorem is that the M.B. distribution, together with those states for which

$$\sum_i \bar{n}_i \left(\dfrac{\Delta n_i}{\bar{n}_i}\right)^2 \lesssim 1$$

occupy almost all of the energy shell.

6. Requirement (a) expresses the property that *any* macroscopic description must have, namely that it must be insensitive to small changes in the position of the phase point P.   That such a "coarse graining" of the Γ-space is necessary for the whole argument was especially emphasized by P. and T. Ehrenfest (l.c. Note 1).   One may say that this coarse graining depends on the observer through his choice of the macroscopic variables.   On the other hand (b) can be looked upon as the requirement imposed by the system (mainly because of the fact that N is very large) on the choice of its macroscopic description.

7. See Khinchin, *Statistical Mechanics*, Chapter II, §5, or E. Hopf, *Ergodentheorie* (Berlin, 1937), or P. R. Halmos, *Lectures on ergodic theory* (Publications of the Mathematical Society of Japan, no. 3, 1956), also for the further mathematical literature. In the following the word "almost" means as usual "except possibly for a set of measure zero".

8. In the physical literature the same idea is expressed by saying that the system must be *quasi-ergodic*. (See P. and T. Ehrenfest, l.c., also for the discussion and criticism of the older ergodic hypothesis of Boltzmann.) By this one means that the trajectory starting from almost any point P will cross in the course of time *any* region around *any* point Q of the energysurface. A metrically transitive system is obviously quasi-ergodic, but the inverse is *not* necessarily true. It may be that the energysurface can be divided in two sets both of finite measure and so interwoven that the points in each set are everywhere dense on the surface. If the orbits starting from points in one set stay in that set then the system is clearly not metrically transitive although it is obviously quasi-ergodic. From the quasi-ergodic property Eq. (19) cannot be deduced. This was attempted by A. Rosenthal (Ann. Physik **43** (1914) 894) and the error was pointed out by A. Melamit (Acta Phys. Polon. **1** (1932) 281).

9. The best known example is the motion of a mass point on a surface of constant negative curvature. That the flow defined by the geodesics on such a surface is metrically transitive was first proved by G. A. Hedlund in 1934 (Ann. of Math. **35** (1934) 787). Compare also E. Hopf, *Ergodentheorie*, Chapter V, and for a simplified proof G. A. Hedlund, Amer. J. Math. **62** (1940) 233.

There is also a paper by Fermi (Physik. Z. **24** (1923) 261) in which a proof is presented of the quasi ergodicity of so-called canonical normal systems with more than two degrees of freedom. These systems were considered by Poincaré (*Les Methodes Nouvelles de la Mecanique Celeste*, Vol. 1, Chapter 5) and they are essentially non-degenerate multiply periodic systems which are perturbed by a potential which is periodic in the angle variables. They include therefore a wide class of mechanical systems, and it would be of great interest to know whether Fermi's argument could be made into a rigorous proof of the metrical transitivity of these systems.

10. Eq. (19) is related to a theorem proved by M. Kac (Bull. Amer. Math. Soc. **53** (1947) 1002) about the *average recurrence time*. Consider again a discrete set of time points $\Delta, 2\Delta, \cdots$ as in the proof of

the Poincaré theorem (Note 4) and an area A on the energysurface. Let $n(P)\Delta$ be the *first* time for a point P in A to return to A, so that $P_n \subset A$. Then for a metrically transitive system Kac proves that the average recurrence time defined by:

$$\bar{n}\Delta = \frac{\Delta}{V(A)} \int \cdots \int_A d\Omega \, n(P)$$

is determined only by the area of A and in fact is equal to $(V/V(A)) \cdot \Delta$. The smaller the area A is, the longer the average recurrence time will be, and the shorter (according to Eq. (19)) the point will spend in the area A.

11. The notion of a normal property of a system was introduced by Jeans (*Dynamical Theory of Gases*, 3rd ed., 1921, p. 74), and was further discussed by Fowler (*Statistical Mechanics*, Cambridge, 1929, §1.4, p. 8). We think that the definition used in the text expresses more precisely what these authors had in mind.

12. This can also be expressed in the following way. Since $D(P, 0)$ corresponds to a given set of values $y_i^{(0)}$ of the macroscopic variables at $t = 0$, one finds by integrating $D(P, t)$ over the different regions on the energy shell corresponding to the different sets of values of the y_i, the conditional probability $P(y_i^{(0)}|y_i, t)$ that at time t the macroscopic variables have the values y_i if at $t = 0$ they have the values $y_i^{(0)}$. For $t \to \infty$, $P(y_i^{(0)}|y_i, t) \to W(y_1, y_2 \cdots)$, where $W(y_1, y_2 \cdots)$ is determiued by the volume of the energy shell corresponding to the set of values $y_1, y_2 \cdots$. Because for large N there is one set of values of the y_i corresponding to an overwhelmingly largest volume, the function $W(y_1, y_2 \cdots)$ will be very sharply peaked at this equilibrium set of values of the y_i.

Formulated in this way the theory becomes completely similar to the *theory of stationary stochastic processes*.

13. This was done first by J. von Neumann (Z. Physik. **57** (1929) 80). For a discussion and criticism of this concept see the article by M. Fierz in the Memorial Volume to Wolfgang Pauli (Interscience Publishers, New York, 1960).

14. It should be pointed out that this terminology is *not* generally used. For instance R. H. Fowler and E. A. Guggenheim (*Statistical Thermodynamics*, Cambridge, 1939, p. 56) call the postulate of the existence of temperature the zeroth law of thermodynamics. Since the

notion of temperature depends, besides on the existence of thermo-
dynamic equilibrium, on the transitive property of the equilibrium state,
and since for the statistical interpretation of the notion of temperature
one needs the canonical ensemble, it seems to us preferable to reserve
the term zeroth law to the fundamental fact of the approach to equili-
brium of a closed system.

15. See for instance: Boltzmann, *Wissenschaftliche Abhandlungen*,
Vol. 1, p. 284; G. Krutkow, Z. Physik. **81** (1933) 377; Khinchin,
Statistical Mechanics, Chapter 5, §19; H. Grad, Comm. Pure Appl.
Math. **5** (1952) 455.

16. It seems very likely therefore that for a system with a large
number of molecules the macroscopic properties of the equilibrium
state can be obtained either from the canonical or from the micro-
canonical ensemble and that the results will always be the same.   From
the point of view of thermodynamics the difference between the two
ensembles lies *only* in the choice of the basic thermodynamic character-
istic function and in the corresponding choice of the macroscopic
variables.   It is difficult though to prove this rigorously and in all
generality, so that it should be verified for any specific problem.

17. This was pointed out clearly in the basic paper by P. Ehrenfest
and V. Trkal (Ann. Physik. **65** (1921) 609).   The neglect of this point
has led to a great deal of discussion and to the so-called "$N!$" con-
troversy.   See for instance E. Schrödinger, *Statistical Thermodynamics*
(Cambridge University Press, 1946) and O. Stern, Revs. Modern
Phys. **11** (1949) 534.

Theory of the Non-Ideal Gas

1. The general problem. We have seen that by computing the partition function $Z(V, T, N)$ we should in principle be able to calculate *all* the macroscopic equilibrium properties of the system when the intermolecular forces are known. Looking now at the experimental
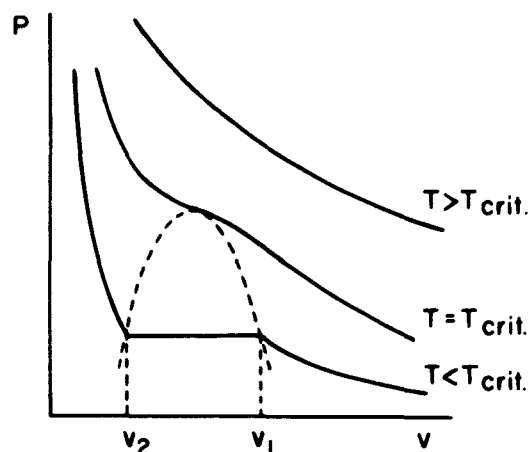

Figure 1

facts, this implies that we should be able to explain the following phenomena:

(a) The deviations from the ideal gas laws which occur when at fixed temperature the volume V is no longer very large compared to Nr_1^3 (r_1 = range of the intermolecular force).

(b) The condensation phenomenon. At low enough temperatures any gas starts to condense at a critical density $1/v_1$, which shows itself in the isotherm by a sharp discontinuity in the slope (see Fig. 1). For $v < v_1$ the pressure stays strictly constant (vapour-liquid equilibrium) till at v_2 one has only the liquid phase. Here there is a second sharp

discontinuity in the slope of the isotherm, and for $v < v_2$ the isotherm rises steeply corresponding to the small compressibility of all liquids.

(c) The existence of a *critical temperature* T_{crit}.   Again for all substances the condensation phenomenon only occurs for $T < T_{crit}$.   If T approaches T_{crit} the horizontal portion of the isotherm becomes shorter and it disappears in the *critical point* C.   For $T > T_{crit}$ there is no longer a discontinuity in the isotherm.

There are other general phenomena.   At still smaller volumes and probably at *any* temperature the substance solidifies, and one has the corresponding solid-liquid and solid-vapour equilibria.[1]   But the explanation of these phenomena from the basic integral $(I, 48)$ for $Z(V, T, N)$ is still so far from being accomplished that I will not bother the reader with other experimental facts.   Before giving a summary of what *has* been accomplished, let us look at the historical background.

2. The theory of van der Waals.   The first great advance in the understanding of the properties of gases and liquids was made by van der Waals in his famous Leiden dissertation of 1873.   Van der Waals tried to take into account the effect of the intermolecular force (attraction at large distance, sharp repulsion at short distance) on the equation of state of the gas and he arrived at the famous equation:

(1)
$$\left(p + \frac{a}{V^2}\right)(V - b) = NkT$$

where a is a measure of the attractive, b of the repulsive forces.[2]   It represents qualitatively all known properties of the gas and liquid phase and especially it "explains" the existence of two phases for $T < T_{crit}$ and the existence of a critical point.   This is shown in the following way.   Since (1) is of the third degree in V, one easily sees that for low enough temperature the isotherm is not monotomic but shows a wiggle (see Fig. 2).   Between the points A and B this must represent an unstable state and hence van der Waals says the system will split in two phases.   One now needs a thermodynamic argument (Maxwell rule or equal area rule) to find the volumes V_1, V_2 of the saturated vapour and liquid and the constant saturated vapour pressure p_s.   The wiggle disappears for $T > T_{crit}$.   The critical point

C is fixed by the fact that there the isotherm has an horizontal inflexion point, so that:

$$\left(\frac{\partial p}{\partial V}\right)_c = \left(\frac{\partial^2 p}{\partial V^2}\right)_c = 0$$

from which follows:

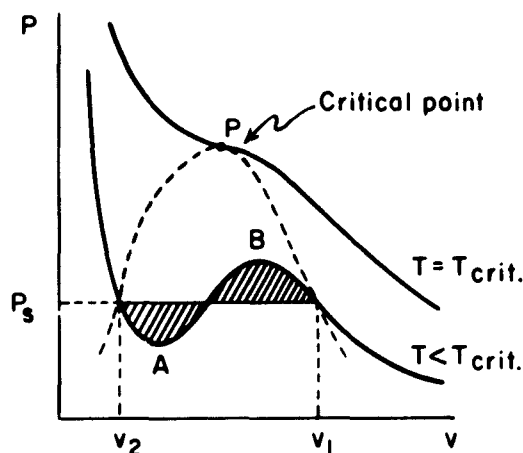(2) $$V_c = 3b, \qquad p_c = \frac{a}{27b^2}, \qquad RT_c = \frac{8a}{27b}.$$

Figure 2

I will not try to review the further remarkable successes of the van der Waals equation. In fact, they were so remarkable that they practically killed the subject for more than fifty years! Let me only still mention that a consequence of (1) is the so-called *law of corresponding states*, which says that if one measures p, V and T with the critical quantities (2) as units, the resulting equation of state is the *same* for all substances. This law, which was instrumental in the precise predictions of Kamerlingh Onnes of all the factors involved in the first liquefaction of Helium, follows from (1) since (1) involves only two constants a and b. The rather general validity of the law indicates that the intermolecular potentials, say for all inert gases, can all be represented by the same equation if one only adjusts the units of length and energy. A good representation of the potential (we will soon see how this can be checked) is for instance the (12,6) Lennard-Jones potential: (see Fig. 3)

$$\phi(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right].$$

From a simple dimensional argument it then follows strictly from $Z(V, T, N)$ that if one measures all lengths in units σ, and the temperature in units ε/k the reduced equation of state should be universal.[3]
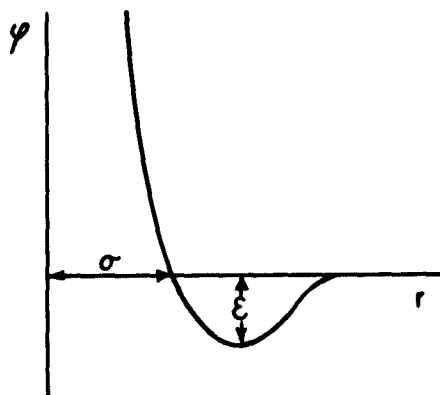

Figure 3

In turn this means that the ratios $V_c/N\sigma^3$ and kT_c/ε should be universal. In fact for the inert gases one finds:

$$\frac{V_c}{2\pi N\sigma^3/3} \simeq 1.50, \qquad \frac{kT_c}{\varepsilon} \simeq 1.25$$

which allows a quick estimate of the strength and range of the inter-molecular potential from the critical quantities.

To come now to the criticism of the van der Waals equation, the point which shows most clearly that the van der Waals equation can *not* be considered as in any way final, is that an additional thermo-dynamic argument is required to fix the saturated vapour pressure. An autonomous statistical theory of the non-ideal gas and the liquid state should not require any thermodynamics. Also, it is clear that since from $Z(V, T, N)$ one should find the state of thermodynamic equilibrium it should be impossible in any bonafide derivation of the equation of state from Z to find unstable or metastable states of the system. In fact we will show in Chapter III that the pressure as derived from Z must be a monotonic non-increasing function of the volume. All "proofs" of the van der Waals and similar equations of state contain therefore necessarily unallowed extrapolations or approximations. Finally there is the failure of the van der Waals equation to describe the phenomena quantitatively correct, although it is unsurpassed qualitatively. Already in 1901, this failure led
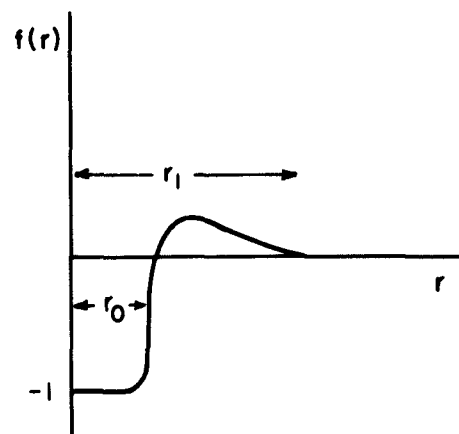
Figure 4

Kamerlingh Onnes to abandon all closed expressions for the equation of state and to represent the data by a series expansion of the form:

$$(3) \qquad \frac{pV}{RT} = 1 + \frac{B(T)}{V} + \frac{C(T)}{V^2} + \cdots.$$

This is called *the virial expansion*; $B(T)$ is the second virial coefficient, $C(T)$ the third, etc.   The representation (3) was not only desperation, but it contained the insight that the successive deviations from the ideal gas law will give information about the interaction of the molecules in pairs, triples, etc.   This has been confirmed by the theoretical derivation of (3) from the partition function Z, first given in all generality by Ursell and Mayer around 1930.[4]   It is a part of the theory which is in a really satisfactory state.

3. The Mayer trick and the connection with the theory of linear graphs. As a first step in the discussion of $Z(V, T, N)$ following Mayer, we introduce:
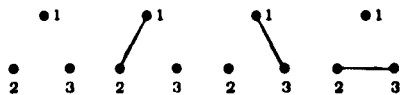
$$(4) \qquad f_{ij} \equiv f(|\mathbf{r}_i - \mathbf{r}_j|) = \exp\left[-\frac{1}{kT}\phi(|\mathbf{r}_i - \mathbf{r}_j|)\right] - 1$$

and rewrite Eq. (48) of Chapter I in the form:

$$(5) \qquad Z(V, T, N) = \frac{1}{N!\lambda^{3N}} \int_V \cdots \int_V d\mathbf{r}_1 \cdots d\mathbf{r}_N \prod_{i<j=2}^{N} (1 + f_{ij}).$$

The general form of the function $f(r)$ is shown in Fig. 4.   Since f_{ij} vanishes when $|\mathbf{r}_i - \mathbf{r}_j|$ is greater than the range r_1 of the forces, an

expansion of the product in (5) will lead to an expansion of Z in powers of V. To see this more in detail, represent each term in the expansion of the product by a linear graph in which each particle is indicated by a point and each factor f_{ij} by a line between the points i and j. For instance for $N = 3$:

$$\prod_{i<j=2}^{3} (1 + f_{ij}) = \quad 1 \quad + \quad f_{12} \quad + \quad f_{13} \quad + \quad f_{23} \quad +$$

(6)

$$+ \quad f_{12}f_{23} \quad + \quad f_{12}f_{13} \quad + \quad f_{13}f_{23} \quad + \quad f_{12}f_{23}f_{31}$$

where we have drawn the graph under each term.   More symbolically for $N = 4$:

$$\prod_{i<j=2}^{4} (1 + f_{ij}) =$$

(1)   (6)   (3)   (12)   (4)

(7)

(12)   (4)   (12)   (3)   (6)   (1)

where the numbers indicate the number of terms represented by each graph if one labels the four points.

Each term in the expansion of (5) corresponds therefore to a particular graph of N labelled points, which in general will consist of a number of disjoint connected parts.   In fact *all* labelled N-point graphs from separate points to the complete graph with $N(N-1)/2$ lines will appear.   Now it is clear that each term in the expansion will lead to a product of integrals, one for each connected part of the corresponding graph.   For example, a point will give the integral:

$$\int_{V} d\mathbf{r} = V$$

a line (i, j) the integral:

$$\int_V \int_V d\mathbf{r}_i \, d\mathbf{r}_j f_{ij}$$

a triangle (i, j, k) the integral:

$$(8) \qquad \int_V \int_V \int_V d\mathbf{r}_i \, d\mathbf{r}_j \, d\mathbf{r}_k f_{ij} f_{ik} f_{jk}$$

and so on. We will call a connected graph also sometimes a *cluster* and the corresponding integral like (8) a *cluster integral*. The advantage of such an expansion of the integrand in (5) is that because of the short range of the forces (beyond which the f_{ij} are zero), the leading term of each cluster integral is proportional to V. It is this feature which has allowed Ursell and Mayer to derive the virial expansion (3) and to find explicit expressions for the virial coefficients in terms of the functions f_{ij}.

4. Some notions of the theory of linear graphs. Since we need some of the simple notions of the theory of graphs, and since part of the terminology I am used to is semi-private, let me collect here all that we will need.[5]

A *linear graph* is a collection of points with lines between certain pairs of points. In general there may be more than one line connecting two points and also loops may occur. If any two points are connected by at most one line and if there are no loops we call the graph *simple* (see Fig. 5). We will mainly have to deal with such graphs. A subset of points which are joined successively by lines is called a *path* connecting the initial and final point. If the final point coincides with the initial point we speak of a *cycle*. A connected graph is one in which there is at least one path between any two points. Otherwise the graph is *disconnected*. It is clearly sufficient to study connected graphs. An *articulation point* is a point where a
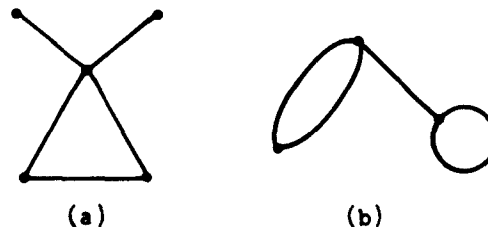

(a)   (b)

Figure 5. (a) simple graphs; (b) not simple graphs

graph can be cut into two or more disconnected parts. A graph without articulation points I call a *star* (see Fig. 6). A general connected graph can be considered as built up out of the constituent stars hung together at the articulation points. If the constituent stars are just single lines we call the graph a *Cayley tree*. It can also be characterized as a connected graph without cycles. If the stars are polygons we will speak of a *Husimi tree*. It is a connected graph in which each line belongs to at most one cycle (see Fig. 7). If more general types of stars are used we will speak of *star trees*. A *pure star tree* is one which consists of only one type of star; otherwise the star tree is *mixed*. Of course if no restrictions are made on the type of stars then the notions of star tree and of connected graph are synonymous.

In the physical applications graphs usually appear as a symbolization of the different terms in a successive approximation method and the number of points usually determines the order of the approximation. In each successive approximation method one can therefore distinguish two problems:

(a) The combinatorial problem: how many "different" terms are there in *n*th order? This can then be expressed by asking how many

(a)   (b)

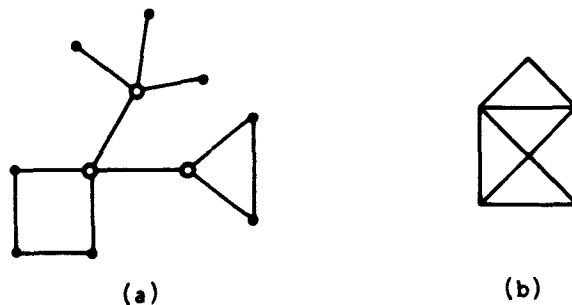Figure 6.   (a) graph with articulation points (small circles); (b) a star

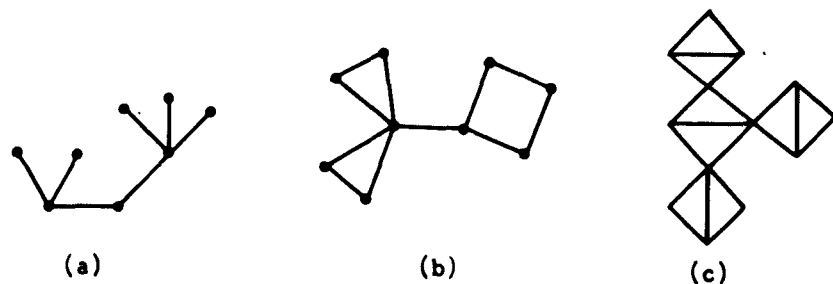(a)   (b)   (c)

Figure 7.   (a) Cayley tree.   (b) Mixed Husimi tree.   (c) Pure star tree.

graphs of n points and of a specific type (as determined by the problem) there are.

(b) The integral problem: what is the contribution or the weight of each graph?

In the combinatorial problem one must distinguish between *labelled graphs* and *free* (or *topological*) graphs. In a labelled graph different points are distinguished by some index. In a free graph the points are regarded as not distinguishable. Of fundamental importance is the number of different labelled graphs corresponding to a given free graph. To enumerate the possibilities one needs the notion of the *group of a graph*. This is defined as the group of automorphisms of the graph, that is the group of the one to one correspondences of the points of the graph which leave the connections invariant. The group can be considered as a permutation group of the points. For example, for an n-gon the group is the dihedral group of order $2n$, and for a so-called *complete* graph of n points (i.e., the graph where all pairs of points are joined by lines) the group is the symmetric group of degree n. The order of the group is the *symmetry number* s of the graph. If one has a free graph of p points and symmetry number s, then there are clearly $p!/s$ different ways in which one can label the points so that one obtains $p!/s$ different labelled graphs.

5. The first Mayer theorem. We now return to the calculation of the partition function $Z(V, T, N)$ as given by (5) and we will consider that the product is expanded and that each term is symbolized by a graph of N labelled points as explained in §3. We also saw that then each term becomes a product of factors each referring to a disjoint connected part of the graph. Mayer showed that the resulting sum of products can be put in a simple form. To derive this, it is illuminating to consider Mayer's result as a special case of the following general theorem.[6]

THEOREM I. *Consider the quantity F_N defined by*:

(9)
$$F_N = \sum_{(G_N)} W(G_N)$$

where the sum goes over all *graphs G_N (connected or disconnected) with N labelled points, and where $W(G_N)$ is a "weight" which is a function of the graph G_N and which is supposed to have the properties:*

(a) *$W(G_N)$ is independent of the labelling of the N points, which means that it only depends on the* free *graph.*

(b) *$W(G_N) = \prod W(C_i)$ where the product goes over all the disjoint*

connected parts C_l of G_N.
Introduce further the quantity:

(10)
$$f_l = \sum_{(C_l)} W(C_l)$$

where the sum runs over all connected graphs with labelled points. The theorem then states that:

(11)
$$1 + F(x) = e^{f(x)}$$

where $F(x)$ and $f(x)$ are the generating functions of the quantities F_N and f_l defined by:

(12)
$$F(x) = \sum_{N=1}^{\infty} F_N \frac{x^N}{N!}, \qquad f(x) = \sum_{l=1}^{\infty} f_l \frac{x^l}{l!}.$$

The proof of the theorem depends on the following fundamental lemma, which we will use over and over again, so that we will formulate and prove it in all generality.

PRODUCT THEOREM. *Consider two arbitrary (finite or infinite) collections $\mathfrak{H}$ and $\mathfrak{G}$ of free graphs and form the product collection $\mathfrak{H} \times \mathfrak{G}$ which consists of all possible pairs of graphs one from $\mathfrak{H}$ and one from $\mathfrak{G}$. Assign weights to each of the graphs in $\mathfrak{H}$ and $\mathfrak{G}$, and assign to each graph of the product collection the product of the weights of the two graphs of which it is formed. If now we* label *the graphs in $\mathfrak{H}$, $\mathfrak{G}$ and $\mathfrak{H} \times \mathfrak{G}$ in all possible different ways and form generating functions similar to (12) (the upper limit can be finite or infinite), then the theorem states that the generating function for the product collection is the product of the generating functions for the two collections $\mathfrak{H}$ and $\mathfrak{G}$.*

PROOF. The total weight assigned to all graphs of p points in collection $\mathfrak{H}$ is:

$$H_p = \sum_i \frac{p!}{s_i} h_i$$

where the sum goes over all different free graphs of p points in $\mathfrak{H}$ and s_i and h_i are the symmetry number and the weight of the ith free graph. Similarly the total weight assigned to all graphs of q points in collection $\mathfrak{G}$ is:

$$G_q = \sum_j \frac{q!}{s_j} g_j$$

For a pair of graphs (i, j) from $\mathfrak{H}$ and $\mathfrak{G}$ the symmetry number is clearly $s_i s_j$. Note that this is so even when the two graphs i and j

are identical, because the operation which transposes the two graphs must *not* be considered as an element of the group of the product graph. Since the weight assigned is $h_i g_j$, it is clear that the total weight assigned to all graphs of N points in the product collection $\mathfrak{H} \times \mathfrak{G}$ is:

$$P_N = \sum_{p+q=N} \frac{(p+q)!}{p!q!} H_p G_q.$$

Hence, defining the generating functions:

$$H(x) = \sum_p H_p \frac{x^p}{p!}, \qquad G(x) = \sum_q G_q \frac{x^q}{q!},$$

$$P(x) = \sum_N P_N \frac{x^N}{N!}$$

it follows that:

$$P(x) = H(x)G(x).$$

This proof makes clear why it is necessary to define the generating functions with the factorials in the denominator.

From the product theorem the proof of Theorem I, that is of Eq. (11), is immediate. If $F_m(x)$ is the generating function for graphs of m disjoint parts then:

$$(13) \qquad F(x) = \sum_{m=1}^{\infty} F_m(x)$$

and from the product theorem follows that:

$$(14) \qquad F_m(x) = \frac{1}{m!} [f(x)]^m$$

where the $m!$ is required because the m parts are chosen from the *same* collection of connected graphs, and any permutation of the m parts leads to the same disjoint graph. From (13) and (14) Eq. (11) follows.

Returning after all this to the partition function $Z(V, T, N)$ it is clear, if one thinks the product expanded, that one can write:

$$(15) \qquad Z(V, T, N) = \frac{1}{N!} \sum_{(G_N)} W(G_N)$$

with:

$$(16) \qquad W(G_N) = \frac{1}{\lambda^{3N}} \int_V \cdots \int_V d\mathbf{r}_1 \cdots d\mathbf{r}_N \prod_{G_N} f_{ij}$$

where the product is over all pairs of points (i, j) which are connected by a line in G_N. Thus if one forms the generating function:

$$(17) \qquad Z_{gr}(V, T, z) = \sum_{N=0}^{\infty} Z(V, T, N)(\lambda^3 z)^N$$

then (except for the λ^3, introduced to cancel the λ^{3N} in (16)) Z_{gr} is clearly similar to $1 + F(x)$ if by convention one puts $Z(V, T, 0) = 1$. The function $Z_{gr}(V, T, z)$ is called the *grand canonical partition function* to distinguish it from the ordinary or canonical partition function $Z(V, T, N)$.

Since clearly the weight $W(G_N)$ defined by (16) fulfills both of the conditions required for the applicability of Theorem I, one can express $Z(V, T, z)$ in terms of the corresponding function for *connected* graphs. Calling (to conform with the usual notation):

$$(18) \qquad b_l(V, T) = \frac{1}{V l!} \int_V \cdots \int_V d\mathbf{r}_1 \cdots d\mathbf{r}_l \sum_{(C_l)} \prod_{C_l} f_{ij}$$

where the product goes over all f_{ij} corresponding to lines in the connected graph C_l and the sum goes over all connected graphs with l labelled points, and calling:

$$(19) \qquad \chi(V, T, z) = \sum_{l=1}^{\infty} b_l(V, T) z^l;$$

then clearly $V\chi(V, T, z)$ is similar to the function $f(x)$ of Theorem I, and hence:

$$(20) \qquad Z_{gr}(V, T, z) \doteq \exp\{V\chi(V, T, z)\}$$

which is the first Mayer relation.[7]

6. The Mayer equations. From (17) and (20) it follows that:

$$(21) \qquad \lambda^{3N} Z(V, T, N) = \frac{1}{2\pi i} \oint dz \, z^{-N-1} \exp\{V\chi(V, T, z)\}.$$

Now note that because of the hard core assumption for the intermolecular potential (see Chapter I, §1), $Z(V, T, N) = 0$ if $N \gtrsim V/(4\pi r_0^3/3)$, so that $Z_{gr}(V, T, z)$ is a polynomial in z with positive coefficients. Therefore $\chi(V, T, z)$ will be a monotonic increasing function of z along the positive real axis. Since z^{-N-1} is a sharply decreasing function, the integrand in (21) will have a steep saddlepoint at some point z_0 on the positive real axis, in the limit that N and V are large such that $Nv = V$ with v fixed. In this limit one can evaluate

(21) by the method of steepest descent.   Call:

$$f(z) = -\ln z + v\chi(Nv, T, z);$$

then one gets in the usual way:

$$\text{(22)} \qquad \lambda^{3N}Z \cong \frac{e^{Nf(z_0)}}{\{2\pi Nf''(z_0)\}^{1/2}}$$

where z_0 is determined by $f'(z_0) = 0$ or:

$$\text{(23)} \qquad \frac{1}{v} = z_0 \frac{\partial}{\partial z_0} \chi(Nv, T, z_0).$$

Now note that for large V and fixed l, $b_l(V, T)$ becomes independent of V.   This is due to the fact that the integrand in (18) consists of a connected set of factors f_{ij}, so that, keeping say $\mathbf{r}_1$ fixed, the integrand will be zero outside a sphere around $\mathbf{r}_1$ of radius of order l times the range of the forces.   Integrating finally over $\mathbf{r}_1$, one sees that because of the factor $1/V$ in (18) the limit:

$$\text{(24)} \qquad \underset{N \to \infty}{\text{Lim}} \, b_l(Nv, T) = b_l(T)$$

exists.   Let us now *assume* that the series (19) for $\chi(Nv, T, z)$ has a finite radius of convergence which for increasing N has a finite lower bound.   Then also the limit series:

$$\text{(25)} \qquad \underset{N \to \infty}{\text{Lim}} \, \chi(Nv, T, z) \equiv \bar{\chi}(T, z) = \sum_{l=1}^{\infty} b_l(T)z^l$$

will have a finite radius of convergence.   Since from (23) follows that for increasing v, z_0 goes to zero, we can make v so large that z_0 is inside the circle of convergence of $\bar{\chi}(T, z)$.   One then obtains from (22) that for large N:

$$\text{(26)} \qquad \Psi = -kT \ln Z = N\left[\psi(v, T) + O\left(\frac{\ln N}{N}\right)\right]$$

with:

$$\text{(27)} \qquad \psi(v, T) = -kT\{v\bar{\chi}(T, z_0) - \ln(\lambda^3 z_0)\}.$$

This verifies the statement made at the end of Chapter I (Eq. (51)) that in the limit the free energy Ψ is proportional to N, so that it is an extensive variable as desired.   In (27) z_0 is determined by:

(28)
$$\frac{1}{v} = z_0 \frac{\partial}{\partial z_0} \bar{\chi}(T, z_0)$$

or:

(A)
$$\frac{1}{v} = \sum_{l=1}^{\infty} l b_l(T) z_0^l.$$

For the equation of state one then obtains:

$$p = -\frac{\partial \psi}{\partial v} = kT \left\{ \bar{\chi}(T, z_0) + v \frac{\partial \bar{\chi}}{\partial z_0} \frac{\partial z_0}{\partial v} - \frac{1}{z_0} \frac{\partial z_0}{\partial v} \right\}$$

so by using (28):

(B)
$$\frac{p}{kT} = \bar{\chi}(T, z_0) = \sum_{l=1}^{\infty} b_l(T) z_0^l.$$

The equations (A) and (B) are the Mayer equations. They determine parametrically the relation between p and v, that is the equation of state. Note still that:

(29)
$$\mu = \psi + pv = kT \ln (\lambda^3 z_0)$$

which shows the thermodynamic meaning of z_0; μ is called the chemical potential.

Since $b_1 \equiv 1$ one gets from (A) that for very large v, $z_0 \simeq 1/v_0$ and then from (B) the ideal gas law follows. Eliminating in this way the z_0 by successive approximation one obtains the Kamerlingh Onnes expansion (3) with:

$$B(T) = -N b_2(T) = -\frac{N}{2} \int d\mathbf{r}_{12} f(r_{12})$$
(30)
$$= 2\pi N \int_0^\infty dr \, r^2 (1 - e^{-\varphi(r)/kT}),$$

$$C(T) = N^2 [-2 b_3(T) + 4(b_2)^2]$$

$$= -\frac{N^2}{3} \int \int d\mathbf{r}_{12} \, d\mathbf{r}_{13} f_{12} f_{13} f_{23}$$
(31)
$$= -\frac{8\pi^2 N^2}{3} \int_0^\infty dr_1 r_1^2 \int_0^\infty dr_2 r_2^2 \int_0^\pi d\theta \sin \theta \, f(r_1) f(r_2)$$
$$\cdot f((r_1^2 + r_2^2 - 2 r_1 r_2 \cos \theta)^{1/2})$$

and so on. This shows explicitly how to find the first few virial coefficients in terms of the intermolecular potential.

The virial coefficients and especially $B(T)$ have been one of the best sources of our knowledge of the intermolecular or van der Waals' forces. To get some idea of the temperature dependence of $B(T)$, suppose that $\phi(r)$ consists of a hard core plus an attraction $\sim r^{-6}$

(see Fig. 8).   Expanding the exponential in (30) one gets approximately

$$B = b - \frac{a}{RT}$$

with $b = 2\pi N r_0^3/3$, $a = 2\pi N^2 \lambda/3d^3$, which is precisely what one would obtain from the van der Waals equation.   As every consequence
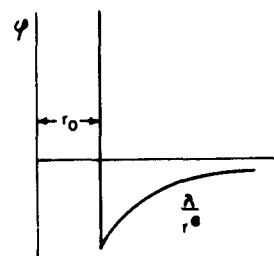

Figure 8

from that equation, this equation represents qualitatively the observed dependence of B on T (see Fig. 9).   Unfortunately $B(T)$ does not determine $\phi(r)$ uniquely, so that one can only make some Ansatz for
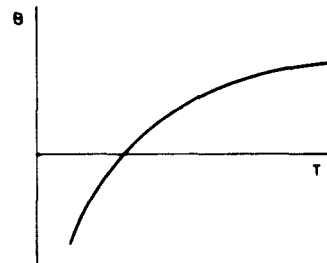
Figure 9

$\phi(r)$ such as the (12-6) Lennard-Jones potential, and then see whether one can adapt the constants ϵ and σ so as to reproduce the observed $B(T)$. A great deal of work[8] has been done in this direction with quite satisfactory results, so that at least for the inert gases one has a good idea of the shape and the strength of the intermolecular force $\phi(r)$. With the $\phi(r)$ obtained from $B(T)$ one then can calculate $C(T)$ and the check with the experimental values is again satisfactory.   This is one of the strong arguments for the assumption that the intermolecular forces are *pair* forces.

7. The second Mayer theorem. The elimination of z_0 between the two Mayer equations (A) and (B) can be done in general and this leads to a striking general expression for the nth virial coefficient which is also due to Mayer. It is based on a theorem, which again we will first formulate and prove in a more general form.

THEOREM II. *Let the weight $W(C_p)$ associated with a connected graph with p labelled points have the properties:*

(a) $W(C_p)$ *is independent of the labelling of the points.*

(b) $W(C_p) = \prod W(S_m)$, *where the product goes over all the stars S_m out of which C_p is constructed.*

Let:

(32)
$$f_p = \sum_{(C_p)} W(C_p), \qquad r_m = \sum_{(S_m)} W(S_m)$$

where the sums go over all different labelled connected graphs of p points, resp. stars of m points. Then the theorem states that:

(33)
$$T(z) = z \exp\left\{\frac{dS(T)}{dT}\right\}$$

where:

(34)
$$T(z) = z\frac{df}{dz} = \sum_{p=1}^{\infty} pf_p\frac{z^p}{p!},$$

(35)
$$S(y) = \sum_{m=2}^{\infty} r_m\frac{y^m}{m!}.$$

PROOF. Consider first, instead of general connected graphs, *pure star trees* in which the single constituent star has q points, weight W and symmetry number s. The generating function $S(y)$ consists then of one term, namely:

(36)
$$S(y) = \frac{q!W}{s}\cdot\frac{y^q}{q!} = \frac{Wy^q}{s}.$$

To construct all possible star trees, it is simplest to consider so-called *rooted* star trees, in which one point (the root) is given besides its label a special designation, say a color. We now build up the star tree from this root. In the rooted star tree, call the stars which have the root point in common the *main leaves*. If $T(z)$ is the generating function for the rooted star trees, then

(37)
$$T(z) = \sum_{n=0}^{\infty} T_n(z)$$

where $T_n(z)$ is the generating function for rooted star trees with n main leaves, and $T_0(z) \equiv z$ counts the single point.

Now we can construct rooted star trees with n main leaves by selecting n rooted star trees with *one* main leaf and hanging them all together on the root. From the product theorem follows:

$$(38) \qquad T_n(z) = \frac{z}{n!} \left[\frac{T_1(z)}{z} \right]^n$$

since $T_1(z)/z$ is the generating function for rooted star trees with one main leaf in which the root point is not counted; the factor z accounts for the common root point and the factor $n!$ is needed because the n parts are chosen from the *same* collection of rooted star trees with one main leaf and any permutation of the n parts leads to the same star tree with n main leaves.

Next one can construct a rooted star tree with one main leaf by hanging $(q - 1)$ general rooted star trees with their roots on the $(q - 1)$ points of the main leaf which are different from the root. Hence applying again the product theorem one has:

$$(39) \qquad T_1(z) = \frac{zqW}{s} [T(z)]^{q-1}.$$

The factor z accounts for the root and W for the weight of the main leaf. The factor q is needed since one can choose any point of the single main leaf as the root point. Finally the factor $1/s$ accounts for the fact that there are s equivalent arrangements of root and $(q - 1)$ rooted star trees on the main leaf because of its symmetry.

Combining (37), (38) and (39) one gets:

$$(40) \qquad T(z) = z \exp\left\{ \frac{qW}{s} \cdot T^{q-1} \right\}$$

and from (36) one sees that in this case:

$$\frac{qW}{s} T^{q-1} = \frac{dS(T)}{dT}.$$

The generalization to *mixed* star trees and therefore to general connected graphs is quite straightforward. In building up the rooted star trees out of rooted star trees with one main leaf, one must now distinguish between the different types of stars which can be the main leaf. Instead of (39) one gets:

$$T_1(z) = \sum_i \frac{zq_i W_i}{s_i} [T(z)]^{q_i - 1}$$

where the sum goes over all types of stars and where each term in the sum counts rooted star trees with one main leaf which is a star of the *i*th type. Instead of (40) one gets:

$$T(z) = z \exp\left\{ \sum_i \frac{q_i W_i}{s_i} T^{q_i - 1} \right\}$$

and since:

$$S(y) = \sum_{m=2}^{\infty} r_m \frac{y^m}{m!} = \sum_i \frac{q_i!}{s_i} W_i \cdot \frac{y^{q_i}}{q_i!}$$

this leads to (33).

Finally the relation:

$$T(z) = z \frac{df}{dz}$$

between the generating functions $f(z)$ and $T(z)$ of connected graphs and rooted connected graphs is obvious since with *labelled* graphs the special designation of *any* point as the root point leads to a *different* rooted graph, so that since the weight is independent of the labelling the total weight of the rooted connected graphs of p points must be $p f_p$.[9]

Let us now return to the Mayer equations. The Mayer weight associated with a connected graph C_p of p points:

(41) $$W(C_p) = \frac{1}{V} \int_V \cdots \int_V d\mathbf{r}_1 \cdots d\mathbf{r}_p \prod_{C_p} f_{ij}$$

has for large V (strictly only in the limit $V \to \infty$) the two properties required for the applicability of Theorem II. The first property is obvious. To prove the second property one integrates in (41) first over all the points of the end point stars in C_p except the articulation points which connect them with the rest of the star tree. Since the f_{ij} depend only on the relative coordinates $\mathbf{r}_i - \mathbf{r}_j$ the result of the integration gives for large V the product of the weights of the end point stars, which will be independent of the coordinates of the articulation points. Continuing this procedure one clearly gets that $W(C_p)$ is the product of the weights of all the stars out of which C_p is constructed.

With (41) $T(z)$ becomes $z\, d\bar{x}/dz$ which is equal to $1/v$ according to Mayer's equation (A). Calling:

(42) $$\beta_{m-1} = \lim_{V \to \infty} \frac{1}{V(m-1)!} \int_V \cdots \int_V d\mathbf{r}_1 \cdots d\mathbf{r}_m \sum_{(S_m)} \prod_{S_m} f_{ij}$$

where the sum goes over all stars with m labelled points, clearly the total weight r_m becomes $(m - 1)!\beta_{m-1}$ and hence:

(43)
$$S'(y) = \frac{d}{dy} \sum_{m=2}^{\infty} r_m \frac{y^m}{m!} = \frac{d}{dy} \sum_{m=2}^{\infty} \frac{y^m}{m} \beta_{m-1}$$
$$= \sum_{v=1}^{\infty} \beta_v y^v \equiv \phi(y).$$

Eq. (34) therefore becomes:

(44)
$$\frac{1}{v} = z_0 \exp\left[\phi\left(\frac{1}{v}\right)\right]$$

which is the expression of the second Mayer theorem. One can say that in (44) by expressing z in $1/v$ one has inverted the first Mayer equation (A). From Mayer's equation (B) one then obtains (calling $1/v = x$)

(45)
$$\frac{p}{kT} = \bar{\chi}(z_0) = \int_0^{z_0} dz \frac{d\bar{\chi}}{dz} = \int_0^{z_0} dz \frac{x}{z}$$
$$= \int_0^z e^{\phi(v)} d(y e^{-\phi(v)}) = x - \int_0^z dy\, y\phi'(y)$$
$$= \frac{1}{v} - \sum_{v=1}^{\infty} \frac{v}{v+1} \beta_v \left(\frac{1}{v}\right)^{v+1}$$

which is the virial expansion. Clearly the nth virial coefficient is:

(46)
$$B_n = -\frac{n-1}{n} \beta_{n-1}$$
$$= -\frac{n-1}{n!} \lim_{V \to \infty} \frac{1}{V} \int_V \cdots \int_V d\mathbf{r}_1 \cdots d\mathbf{r}_n \sum_{(S_n)} \prod_{S_n} f_{ij}.$$

The expressions (30) and (31) for the second and third virial coefficient are special cases of (46). For the fourth virial coefficient (46) gives:

$$B_4 = -\frac{1}{8V} \lim_{V \to \infty} \int \cdots \int d\mathbf{r}_1 \cdots d\mathbf{r}_4 \left\{ \underset{(3)}{\square} + \underset{(6)}{\boxslash} + \underset{(1)}{\boxtimes} \right\}$$

where the numbers refer to the numbers of terms of the types symbolized by the graphs.

Finally one should emphasize that such a general expression for the virial coefficients can *only* be derived when the intermolecular forces are *pair forces* or have the *additivity property*. For non-additive forces (and therefore in the quantum theory!) the Mayer equations (A) and (B) are still valid with the appropriate definition of the b_l, but the virial expansion can only be obtained by the successive elimination of the parameter z_0.

8. The convergence question and the Gaussian model. I mentioned in §6 that one *assumes* that the radius of convergence of the series (19) for $\chi(Nv, T, z)$ has for increasing N a finite lower bound which is then the radius of convergence of the Mayer series:

$$\bar{\chi}(T, z) = \sum_{l=1}^{\infty} b_l(T)z^l$$

which implies that also the virial series has a finite radius of convergence. I think that all this is very likely to be true but a strict proof does not exist.[10] It is clear that everything will depend on the form of the intermolecular force $\phi(r)$. If $\phi(r)$ has a hard core, then we saw already that $Z_{gr}(V, T, z)$ is a polynomial in z with positive coefficients starting from one. Since:

$$\chi(V, T, z) = \sum_{l=1}^{\infty} b_l(V, T)z^l = \frac{1}{V} \ln Z_{gr}(V, T, z)$$

clearly $\chi(V, T, z)$ will have for any V a finite radius of convergence, which is determined by the zero of $Z_{gr}(z)$ closest to the origin. What happens for $V \to \infty$, and also for other molecular forces in which say $\phi(r) \sim r^{-n}$ for small r (as in the Lennard-Jones potential), is not known and seems to me difficult to settle without having an idea about the behaviour of the b_l for large l. For this reason we have tried to investigate the asymptotic behaviour of the b_l for a special model, the so-called *Gaussian model*, and although we have not reached any definite results, it seems to me that the mathematical problems one runs into are so intriguing, that they warrant a short discussion.[11]

For a purely repulsive potential $\phi(r)$, the Mayer function $f(r)$ will always be negative and will look as shown in Fig. 10. For a soft repulsion it is then tempting to replace f_{ij} by the Gaussian function:

(47) $$f_{ij} = -\exp[-\alpha|\mathbf{r}_i - \mathbf{r}_j|^2].$$

Mind that this does *not* correspond to a real physical potential, since with (47) $\phi(r)$ would be temperature dependent. But if we are
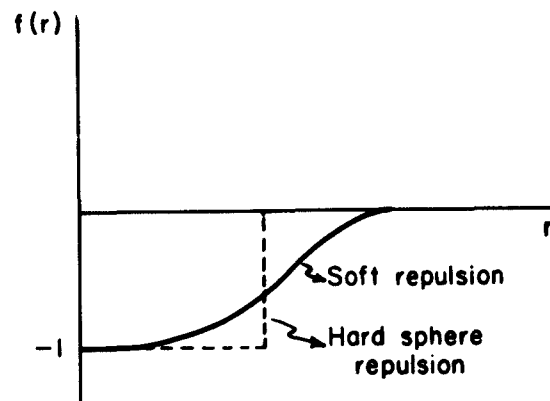
Figure 10

interested only in the behaviour of the gas at *fixed* temperature, (47) should represent qualitatively the effect of a soft repulsive potential.

With (47) all cluster integrals can of course be performed. It is even possible to do this for a finite volume if we put the gas in a Gaussian vessel, that is if we represent the effect of the walls of the vessel by a Gaussian potential $\exp(-\beta r^2)$, corresponding to a "volume" $(\pi/\beta)^{3/2}$ and of course with $\beta \ll \alpha$. However, we have looked mainly at the limit $V \to \infty$, that is at $b_l(T)$. It is easy to show that in this case the weight (41) becomes:

$$(48) \qquad W(C_p) = (-1)^k \left(\frac{\pi}{\alpha}\right)^{3(p-1)/2} [d(C_p)]^{-3/2}$$

where k is the number of lines in C_p, and where $d(C_p)$ is the so-called *graph complexity*. This is defined in terms of the *graph matrix* $d_{ij}(C_p)$, which is a p by p matrix with elements defined by:

$$d_{ij} = \begin{cases} -1 & \text{if the line } (i, j) \text{ occurs in } C_p \\ 0 & \text{otherwise} \end{cases} \qquad (i \neq j)$$

$d_{ii} =$ degree of the point i in C_p, that is the number of lines incident on i.

It is easy to see that the determinant $\|d_{ij}\|$ is zero and that all minors of order $(p-1)$ are equal. Their common value is the graph complexity. Eq. (48) shows that the weight of the graph becomes smaller in absolute value the more complex the graph is, which is clearly as it should be. It is also of interest to note the explicit dependence of $W(C_p)$ on the number of dimensions.

Many properties of graph matrices are known, but let me only mention the following two theorems:[12]

(a) The graph complexity $d(C_p)$ is equal to the number of labelled Cayley trees of p points which are subgraphs of C_p.

(b) The sum of the complexities for all graphs C_{pk} of p labelled points and k lines is given by:

$$\text{(49)} \qquad \sum_{(C_{pk})} d(C_{pk}) = p^{p-2} \binom{\frac{1}{2}(p-1)(p-2)}{k-p+1}.$$

Clearly if we would know the distribution of the values of the graph complexity for all connected graphs of p points and k lines, then one would be able to find an explicit expression for b_p. In fact, if $n(p, k, d)$ is the number of graphs of p points, k lines and complexity d, then from (48) and the definition of b_p it follows that:

$$\text{(50)} \qquad b_p = (2b)^{p-1} \frac{1}{p!} \sum_{k=p-1}^{p(p-1)/2} (-1)^k \sum_d \frac{n(p,k,d)}{d^{3/2}}$$

where:

$$b = \frac{1}{2}\left(\frac{\pi}{\alpha}\right)^{3/2}$$

is the analogue of the van der Waals' b for this case (since $b_2 = -b$) and where the sum over k goes over all the possible numbers of lines which can occur in a connected graph of p points. Of course, for finite p and k only a discrete set of values of d is possible so that $n(p, k, d)$ is a step function, but if p increases and for k in the middle of its range actual numerical experience (all complexities for graphs up to $p = 7$ have been computed)[13] suggests that $n(p, k, d)$ becomes a genuine smooth distribution function which in fact seems Gaussian around its average value. It would be of great interest, I think, if these statements could be proved. Unfortunately at present all we know about the distribution are the zeroth and first moments, since:

$$\sum_d n(p, k, d) = C_{pk}$$

where C_{pk}, the number of connected (p, k) graphs can be found from (c), Note 7, and:

$$\sum_d dn(p, k, d) = p^{p-2} \binom{\frac{1}{2}(p-1)(p-2)}{k-p+1}$$

which is a rewriting of (49). We have been unable to compute higher moments. Already the second would be worth knowing!

1. The equilibrium pressures of the solid-vapour (sublimation), solid-liquid (melting) and liquid-vapour (evaporation) equilibria as function of the temperature meet in the *triple point A* and divide the (p, T) plane into three regions (see Fig. a). We saw that the liquid-vapour line stops at the critical point. It is therefore possible, by going around the critical point, to change the vapour into a liquid
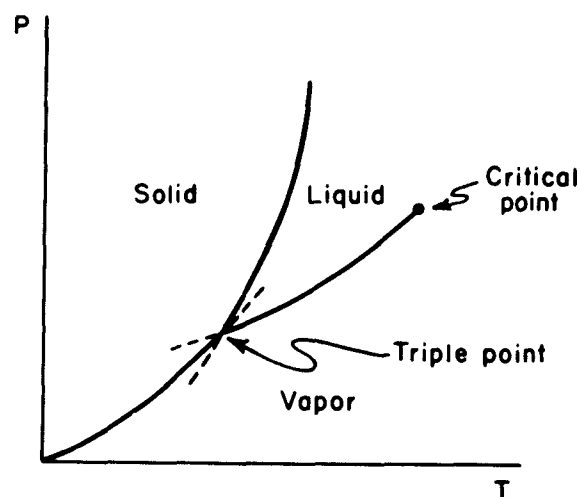

Figure a

without ever having the two phases at the same time. One can make a *continuous* transition from the vapour to the liquid state. At present it is unknown whether the same is true for the fluid and the solid state, or in other words whether the melting line *AB* stops in a second critical point. It seems unlikely, because, as Landau has pointed out, a solid and a fluid are qualitatively different. A fluid is just a very dense gas, but in a solid there is a long range order in the positions of the molecules, and it is difficult to imagine how this could develop gradually from the random arrangement of the molecules in a gas. Experimentally it is known that in some cases the melting line goes to much higher temperatures than T_{crit}. One can solidify

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Helium by high pressures at 50°K, which is about ten times the critical temperature.

2. The various "derivations" of the van der Waals equation have in common that the effect of the repulsive forces (the "b" correction) and the effect of the attractive forces (the "a" correction) are treated separately.   One can argue for instance as follows:

Omitting the attractive forces and taking the repulsive force as between elastic spheres of diameter d, the partition function becomes:

(a)
$$Z = \frac{1}{N!\lambda^{3N}} \int_V \cdots \int_V d\mathbf{r}_1 \cdots d\mathbf{r}_N \prod_{i<j} S(|\mathbf{r}_i - \mathbf{r}_j|)$$

where

$$S(r_{ij}) = \begin{cases} 0 & \text{if } r_{ij} < d, \\ 1 & \text{if } r_{ij} > d. \end{cases}$$

This means that one has to find the volume of a $3N$ dimensional cube (taking V cubical) from which are excluded the cylindrical regions $|\mathbf{r}_i - \mathbf{r}_j| \leq d$.   This is a very difficult problem!   However, if $V \gg Nv_0$ where $v_0 = 4\pi d^3/3$, then in first approximation one can neglect the overlapping of the action spheres, so that the integral in (a) becomes:

$$J = V(V - v_0)(V - 2v_0) \cdots (V - (N - 1)v_0)$$

$$= V^N \prod_{s=1}^{N-1} \left(1 - \frac{sv_0}{V}\right).$$

Hence:

$$\ln J = N \ln V + \sum_{s=1}^{N-1} \ln \left(1 - \frac{sv_0}{V}\right)$$

$$\simeq N \ln V - \sum_{s=1}^{N} \frac{sv_0}{V}$$

$$= N \ln V - \frac{N^2 v_0}{2V} \simeq N \ln (V - b)$$

if $b = Nv_0/2 = 4 \times$ proper volume of the molecules.   Therefore $J = (V - b)^N$ and we will keep this form even when V is *not* large compared to b.

Now, to take into account the attractive forces, one can say that if the range of these forces is sufficiently long, the average potential

energy will be $-CN^2/2V$, since each molecule attracts all molecules in its action sphere and the number of these molecules will be proportional to the number density N/V. C is a positive constant and the contribution to the partition function is therefore roughly $\exp(+a/VkT)$ with $a = CN^2/2$. Altogether one gets therefore:

(b)
$$Z = \frac{1}{N!\lambda^{3N}} e^{a/VkT} (V - b)^N$$

and from $p = kT\partial(\ln Z)/\partial V$ van der Waals equation follows.

3. This was first pointed out by J. de Boer (Dissertation, Amsterdam, 1940; Physica **14** (1948) 139). It is important to note that the mass of the molecule does not affect the equation of state in the classical theory to which we restrict ourselves. In the quantum theory this is no longer true. The equation of state, using the same intermolecular potential, then depends on a third dimensionless variable, the so-called de Boer parameter:

$$\Lambda = \frac{h}{\sigma(m\varepsilon)^{1/2}}.$$

See also the dissertation of R. J. Lunbeck (Amsterdam, 1951).

4. H. D. Ursell, Proc. Cambridge Philos. Soc. **23** (1927) 685. The work of Mayer is summarized in the book of J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (Wiley, New York, 1940). For the generalization to the quantum theory see B. Kahn and G. E. Uhlenbeck, Physica **5** (1938) 399; B. Kahn (Dissertation, Utrecht, 1938). For the generalization to the Bose or Fermi statistics see T. D. Lee and C. N. Yang, Phys. Rev. **113** (1959) 1165.

5. Most of the terminology is the same as in the book of König (*Theorie der Endlichen und Unendlichen Graphen*, Leipzig, 1936). There is no special term for a graph without articulation points, and it is convenient to have one. The word *star* and the corresponding notion of *star tree* were introduced in our paper on the combinatorial problems in the theory of graphs (Proc. Nat. Acad. Sci. U.S.A. **42** (1956) 122).

6. The following presentation of the Mayer theory follows a review article by G. W. Ford and G. E. Uhlenbeck entitled: *The theory of linear graphs with applications to the theory of the virial development of the properties of gases*, which appears in *Studies in statistical*

mechanics Vol. I (North Holland Publishing Company, Amsterdam, 1962).

7. If one takes in Theorem I for the weight W, y^k, where y is an arbitrary variable and k is the number of lines in the graph G_N or C_l, then it is clear that W fulfills all the requirements, and that therefore Theorem I is applicable.   One obtains:

(c) $$1 + N(x, y) = e^{C(x,y)}$$

where:

(d) $$N(x, y) = \sum_{p=1}^{\infty} \frac{x^p}{p!} \sum_{k=0}^{p(p-1)/2} N_{pk}y^k,$$

(e) $$C(x, y) = \sum_{p=1}^{\infty} \frac{x^p}{p!} \sum_{k=p-1}^{p(p-1)/2} C_{pk}y^k$$

and:

N_{pk} = number of labelled (p, k) graphs (= graphs of p points and k lines)

(f) $$= \binom{p(p-1)/2}{k},$$

C_{pk} = number of connected, labelled (p, k) graphs.

Eq. (c) was first derived by R. J. Riddell (Dissertation, University of Michigan, 1951).   It allows the calculation of the numbers C_{pk} in terms of the known binomial coefficients N_{pk}.

8. For a complete account see the book by J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, *The Molecular Theory of Gases and Liquids* (Wiley, New York, 1954).   A very useful summary of the theoretical calculations of the virial coefficients is given by T. Kihara, Revs. Modern Phys. **25** (1953) 831; **27** (1955) 412.

9. By taking as in Note 7 for the weight W, y^k (k = number of lines in the graph) one sees that the two requirements for the weight $W(C_p)$ are fulfilled so that Theorem II is applicable.   Writing:

(g) $$S(x, y) = \sum_{p=2}^{\infty} \frac{x^p}{p!} \sum_{k=p-1}^{p(p-1)/2} S_{pk}y^k$$

where S_{pk} is the number of stars with p labelled points and k lines (with the convention $S_{21} = 1$), and putting:

$$z(x, y) = x \frac{\partial}{\partial x} C(x, y)$$

where $C(x, y)$ is given by (e), then Theorem II yields the second Riddell formula:

(h)
$$\frac{\partial}{\partial z} S(z, y) = \ln \frac{z}{x}.$$

From (h) one can find S_{pk} in terms of the C_{pk}. It is not difficult to show that for large p and $k > p \ln p$ the numbers N_{pk}, C_{pk} and S_{pk} are asymptotically equal, so that one can say that for large p and $k > p \ln p$ the overwhelming majority of the graphs are stars.

10. For a time the convergence question seemed (even to the physicist!) of great interest because Mayer, Kahn and Uhlenbeck (see Note 4 for the literature) had speculated and had tried to prove that the nearest singularity of $\bar{\chi}(T, z)$ on the positive real z-axis (assuming that there $\bar{\chi}$ and $d\bar{\chi}/dz$ remain finite) would determine the point of condensation of the gas. This was strongly suggested by the case of the ideal Bose gas, which is of course *not* a special case of the non-ideal gas theory we have discussed (since the deviations of the ideal gas laws are in this case due to quantum effects), but which *is* a case for which the corresponding b_l can be evaluated explicitly. In fact, already in 1925 Einstein derived for the Bose gas the equations:

$$\frac{1}{v} = \frac{1}{\lambda^3} \sum_{l=1}^{\infty} \frac{A^l}{l^{3/2}},$$

(i)

$$\frac{p}{kT} = \frac{1}{\lambda^3} \sum_{l=1}^{\infty} \frac{A^l}{l^{5/2}}$$

which have precisely the same form as the Mayer equations if one puts:

$$z = \frac{A}{\lambda^3}, \qquad b_l(T) = \frac{\lambda^{3(l-1)}}{l^{5/2}}.$$

Clearly the series:

$$\bar{\chi}(A) = \sum_{l=1}^{\infty} \frac{A^l}{l^{5/2}}$$

is convergent up to $A = 1$, which is the nearest singularity on the positive real axis of the analytic function generated by the series. The point $A = 1$ is a branchpoint of order two and $\bar{\chi}$ and $d\bar{\chi}/dA$ are finite at this point. It is known, and it can be proved in various ways, that

at this point a phase transition occurs, the so-called Bose-Einstein condensation.   For values of v smaller than:

$$v_1 = \frac{\lambda^3}{\sum l^{-5/2}} = \frac{\lambda^3}{2.612\cdots}$$

the pressure stays strictly constant till $v = 0$. Also the convergence of the virial series which follows from (i) by eliminating A has been investigated and it has been shown (W. H. J. Fuchs, J. Rational Mech. Anal. 4 (1955) 647) that the virial series converges *beyond* the condensation point. In fact Fuchs could show that the radius of convergence of the virial series (in λ^3/v) lies between 12.56 and 27.73.

Unfortunately, by now it seems very likely that the connection between the condensation point and the singularity on the positive real axis of the function $\bar{\chi}$ for the ideal Bose gas is a kind of remarkable fluke, and that for real gases there is *no* such a direct connection. We come back to this point in Chapter III.

11. To our knowledge the first use of the Gaussian model was by E. W. Montroll, T. H. Berlin, and R. W. Hart. The article appears in *Changements de phases*, Société de Chimie Physique, Paris, 1952, p. 212.

12. The first theorem is due to Kirchhoff (*Gesammelte Abhandlungen*, Leipzig, J. Barth, 1882, p. 22). If one takes for C_p the complete graph of p points, which has the complexity:

$$\begin{vmatrix} p-1 & -1 & \cdots & -1 \\ -1 & p-1 & \cdots & -1 \\ \vdots & \vdots & & \vdots \\ -1 & -1 & \cdots & p-1 \end{vmatrix} = p^{p-2}$$

then this must therefore be the number of Cayley trees with p labelled points, which is a well known result first derived by Cayley.

The second theorem is due to G. W. Ford. It can be proved in the following way.   From the Kirchhoff theorem follows that one can write:

$$\sum_{(C_{pk})} d(C_{pk}) = \sum_{(T_p)} \sum_{(C_{pk}) \supset T_p} 1$$

where the first sum is over all Cayley trees of p points and the second sum is over those (p, k) graphs which contain a given Cayley tree T_p. Now the number of connected graphs with p labelled points and k lines which contain a particular Cayley tree is just the number of ways $(k - p + 1)$ lines can be distributed among the $(1/2)(p - 1)(p - 2)$ pairs of points in the Cayley tree which have no line.   Therefore:

$$\sum_{(C_{pk}) \gtrless T_p} 1 = \begin{pmatrix} \frac{1}{2}(p-1)(p-2) \\ k - p + 1 \end{pmatrix}$$

and since there are p^{p-2} Cayley trees with p points, Eq. (49) follows.

13. For tables see the article referred to in Note 6. Note, that one can formulate the problem of finding the distribution function $n(p, k, d)$ also in the following way. Find the distribution of the first principal minor of *random, symmetric p by p matrices* in which with equal a priori probability k of the $p(p-1)/2$ off-diagonal elements, say on the right of the main diagonal, are set equal to minus one and the rest equal to zero. The matrix is then completed by taking each diagonal element equal to the sum of the elements on the corresponding row (or column) with the opposite sign.

Remarks on the Condensation Problem

1. Introduction. Although the phenomena of condensation and other phase transitions (like melting) are so very familiar, they are, when one tries to think about them, rather mysterious. How do the molecules of the vapour "know" that at a definite specific volume
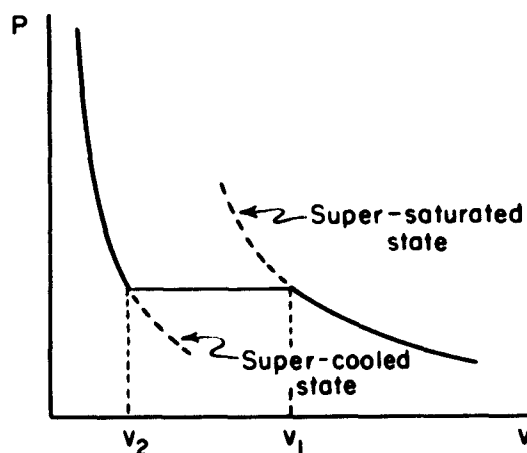

Figure 1

they should condense and form two phases? And why is the transition so sharp? Clearly there are two arrangements of the molecules with "probabilities" depending on v which switch over at the critical value v_1. This is confirmed by the phenomena of supersaturation and supercooling, represented by extensions of the vapour and liquid parts of the isotherm and in which the vapour and liquid are in metastable states (see Fig. 1). For van der Waals these phenomena are of course no mystery and in fact seem to confirm his views. However, once one gives up the van der Waals equation this picture makes one doubt whether the condensation phenomenon *can* come out from the basic equation:

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(1) $e^{-\beta\Psi} = Z = \dfrac{1}{N!\lambda^{3N}} \displaystyle\int_V \cdots \int_V d\mathbf{r}_1 \cdots d\mathbf{r}_N \exp[-\beta \sum_{i<j} \phi(r_{ij})]$

where $\beta = 1/kT$.

At one time people thought that perhaps the stable isotherm could not be derived from (1) without further assumptions. Perhaps one should make a separate calculation of Ψ for two different arrangements of the molecules, one corresponding to a homogeneous phase and one corresponding to the two phase system. For each volume one would then obtain two values of Ψ and the real isotherm would be determined by the lowest value of Ψ. Although such calculations for phase transitions between different *solid* phases have given good results, it is I think now the accepted opinion that they are in principle not correct. The integral (1) should *always* give the most probable state of the system, which is the state of stable equilibrium. The stable isotherm should therefore follow *automatically* from (1) without further assumptions.

However, from the mathematical standpoint it is hard to imagine how the harmless Eq. (1) could lead to a Ψ (and therefore to a p) with such sharp discontinuities. The answer to this lies in the fact that one is interested in a *limit property* of Ψ. The problem has a physical sense only when the system is very large. One is therefore led to the investigation of the limit $N \to \infty$, $V \to \infty$, $v = V/N$ finite. One can then prove that the limit:

(2) $$\psi(v, T) = \lim_{N\to\infty} \frac{1}{N}\, \Psi(Nv, T, N)$$

always exists. It is for this function $\psi(v, T)$ that one should expect the sharp discontinuities, and although perhaps still surprising (and certainly not proved) it is clearly mathematically conceivable.

Finally, how about the supersaturation phenomenon? If (1) gives the stable isotherm, then it can *not* explain supersaturation. To explain this strictly from the partition function one must think of situations in which the supersaturated vapour is in an equilibrium state. This is the case in capillary vessels, and for the strict explanation of supersaturation a detailed study of the effect of the *shape* of the vessel would therefore be necessary. It has never been really attempted.

2. The Van Hove theorem.[1]   I said already that one can show that the limit (2) exists. This was proved rigorously first by L. Van Hove who could in addition show that $p = -\partial\psi/\partial v$ is a monotonic decreasing function (or better a never increasing function) of v. This con-

firms therefore that one never can ʁ∈ʟ ∢ van der Waals like isotherm from (1), but of course it does not show that there must be a horizontal portion in the isotherm.

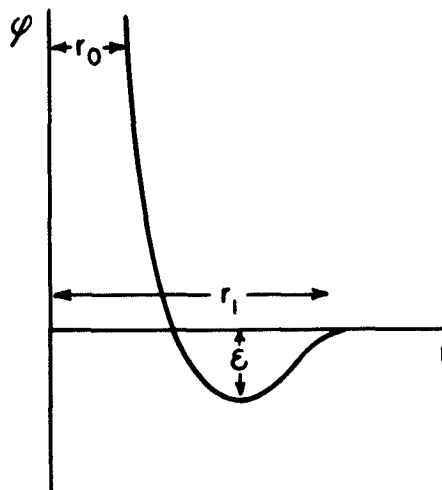A simplified proof of these results which probably can be made rigorous goes as follows.

Figure 2

Assume that $\phi(r)$ has a hard core r_0, and that for $r > r_0$ the force is attractive, range r_1 and with a lower bound for the potential equal to $-\epsilon$ (see Fig. 2). I am sure that these special assumptions can be relaxed, but let me stick to them. Now divide the (cubical) volume $V = L^3$ in cubical cells each of volume $\gamma = d^3$ where $L \gg d \gg r_1$. The idea of the proof consists of comparing the integral (1) with the value it would have if we eliminate all the interactions between the particles in different cells. Write in this case for the integral

$$(3) \qquad \tilde{Z} = \frac{1}{N!\lambda^{3N}} \int_V \cdots \int_V d\mathbf{r}_1 \cdots d\mathbf{r}_N \, e^{-\beta\tilde{\Phi}} \equiv \exp[-\beta\tilde{\Psi}(V, T, N)].$$

$\tilde{\Phi}$ is the new total potential energy, and call $\Phi = \sum_{i<j} \phi(r_{ij})$ the original potential energy. Since with our assumptions the interaction between cells is attractive $\tilde{\Phi} > \Phi$. On the other hand since each cell is surrounded by a layer of volume $6d^2r_1$ in which there can be external molecules with which it can interact, and since in this layer there can be at most d^2r_1/r_0^3 molecules (omitting all numerical factors), and since each of these molecules can interact at most with r_1^3/r_0^3 other molecules, one must have (since there are V/d^3 cells):

$$\Phi \geqq -\frac{d^2 r_1}{r_0^3}\cdot\frac{r_1^3}{r_0^3}\cdot\frac{V}{d^3}\cdot\varepsilon + \tilde{\Phi}.$$

Hence one can conclude:

$$e^{-\beta\tilde{\Phi}} \leqq e^{-\beta\Phi} \leqq \exp[-\beta\tilde{\Phi} + \rho\beta V/d]$$

with $\rho = r_1^4\varepsilon/r_0^6$. The integration over $r_1\cdots r_N$ does not change the direction of the inequalities and by calculating the free energies Ψ and $\tilde{\Psi}$ one obtains:

$$(4) \qquad \frac{1}{N}\,\tilde{\Psi} \geqq \frac{1}{N}\,\Psi \geqq \frac{1}{N}\,\tilde{\Psi} + \frac{\beta\rho v}{d}$$

where $v = V/N$. Since increasing N, keeping v fixed, one still can let $d \to \infty$ say as $N^{1.6}$, one sees that $\tilde{\Psi}/N$ and Ψ/N will approach to the same limit if such a limit exists. Now

$$(5) \qquad \begin{aligned} \tilde{Z} &= \frac{1}{N!\lambda^{3N}}\,\underset{(n_i)}{S'}\,\frac{N!}{n_1!n_2!\cdots n_\nu!}\,\prod_{i=1}^{\nu}\int_\gamma\cdots\int_\gamma d\mathbf{r}_1\cdots d\mathbf{r}_{n_i}\,\exp[-\beta\Phi(\mathbf{r}_1\cdots\mathbf{r}_{n_i})] \\ &= \underset{(n_i)}{S'}\,\exp[-\beta\sum_{i=1}^{\nu}n_i\psi(n_i,\gamma)] \end{aligned}$$

where the sum is over all numbers n_i of particles in the ith cell, with the condition (indicated by the prime):

$$\sum_i n_i = N,$$

and where we have put:

$$(6) \qquad e^{-\beta n_i\psi(n_i,\gamma)} = \frac{1}{n_i!\lambda^{3n_i}}\int_\gamma\cdots\int_\gamma d\mathbf{r}_1\cdots d\mathbf{r}_{n_i}\,\exp[-\beta\Phi(\mathbf{r}_1\cdots\mathbf{r}_{n_i})].$$

Many of the numbers n_i may still be equal to each other. Let a_k be the number of cells in which the number of molecules is k, then

$$(7) \qquad \tilde{Z} = \underset{(a_k)}{S''}\,\frac{\nu!}{\prod a_k!}\,\exp[-\beta\sum_k ka_k\psi(k,\gamma)]$$

where the double prime indicates the conditions:

$$(8) \qquad \sum_k a_k = \nu, \qquad \sum_k ka_k = N.$$

Calling:

$$g_k = e^{-\beta k\psi(k,\gamma)}$$

one sees that (7) is of the multinomial form and one knows that for ν

and N large it is closely approximated by the maximum term in the sum, for which:

(9) $$a_k = Ag_k z^k$$

where A and z must be determined from (8).   In fact:

(10) $$\ln \bar{Z} \cong -N \ln z + \nu \ln \sigma(z)$$

with:

$$\sigma(z) = \sum_k g_k z^k.$$

From (8) and (9):

$$\nu = A\sigma(z), \qquad N = Az\frac{d\sigma}{dz}$$

so that since $\nu = V/d^3 = N v/d^3$, one has:

(11) $$\frac{v}{d^3} = \frac{\sigma}{z(d\sigma/dz)}.$$

For fixed d, z depends therefore only on v and from (9) it then follows (always for fixed d) that:

(12) $$\frac{1}{N}\ln \bar{Z} \cong -\ln z + \frac{v}{d^3}\ln \sigma(z) = -\beta\psi(v).$$

Together with the inequality (4), this shows that the limit (2) exists. Furthermore from the inequality (4) it follows that also $p = -\partial\psi/\partial v$ and $\tilde{p} = \partial\psi/\partial v$ differ at most by a constant quantity proportional to $1/d$, and which can therefore be made as small as one wishes.   So it is sufficient to look at $\tilde{p}$.   From (12) follows:

$$\tilde{p} = \frac{1}{\beta d^3}\ln \sigma(z),$$

(13)

$$\frac{\partial\tilde{p}}{\partial v} = \frac{1}{\beta d^3}\frac{d\ln \sigma(z)}{dz}\frac{dz}{dv}$$

and from (11) one gets:

(14) $$\frac{dv}{dz} = \frac{d^3}{z^3(d\sigma/dz)^2}\left[z^2\left(\frac{d\sigma}{dz}\right)^2 - \sigma z\frac{d}{dz}\left(z\frac{d\sigma}{dz}\right)\right]$$

$$= \frac{d^3}{z^3(d\sigma/dz)^2}\left[\left(\sum_k kg_k z^k\right)^2 - \left(\sum_k g_k z^k\right)\left(\sum_k k^2 g_k z^k\right)\right]$$

$$= -\frac{d^3}{2z^3(d\sigma/dz)^2}\sum_{k,j}(k-j)^2 g_k g_j z^{k+j} \leqq 0.$$

Since all $g_k > 0$, one sees from (13) that the sign of $\partial p / \partial v$ is determined by dz/dv, and from (14) one can then conclude that $\partial \bar{p} / \partial v$ and therefore $\partial p / \partial v < 0$, which is the content of the second part of the Van Hove theorem.[2]

3. The ideas of Yang and Lee. In a very interesting paper[3] Yang and Lee have shown a way how the condensation phenomenon could follow mathematically from the basic equation (1) in the limit $N, V \to \infty$, $v = V/N$ fixed. Their starting point is the grand canonical partition function:

$$Z_{gr}(V, T, z) = \sum_{N=0}^{\infty} (\lambda^3 z)^N Z(V, T, N)$$

for which we derived in Chapter II the expression:

$$(15) \qquad Z_{gr}(V, T, z) = \exp\{V\chi(V, T, z)\}$$

which is valid for any finite V. With the assumption of a hard core, radius r_0, we already noted that Z_{gr} must be a polynomial of degree $M \simeq V/r_0^3$. Let the zeros of this polynomial be z_i, then (dropping from now on the T, which remains constant anyway):

$$(16) \qquad Z_{gr}(V, z) = \prod_{i=1}^{M} \left(1 - \frac{z}{z_i}\right)$$

and

$$(17) \qquad \chi(V, z) = \frac{1}{V} \sum_{i=1}^{M} \ln\left(1 - \frac{z}{z_i}\right).$$

One can therefore interpret $\chi(V, z)$ as the complex logarithmic potential of M point charges of strength $1/V$ situated at the points z_i. Note that since the coefficients of the polynomial $Z_{gr}(V, z)$ are positive, none of the zeros z_i can be on the positive real axis, so that $\chi(V, z)$, for fixed V, will be an analytic function of z along the positive real axis.

Let us now look at the limit $V \to \infty$. For increasing V the strength of the charges become smaller and smaller, while the number M increases. *Suppose* now that in the limit $V \to \infty$ a number of the point charges concentrate themselves in a *single layer AB which crosses the positive real axis*. Of course in addition there may be other layers like CD and finite poles $P_1, P_2, \cdots$ (see Fig. 3). The function:

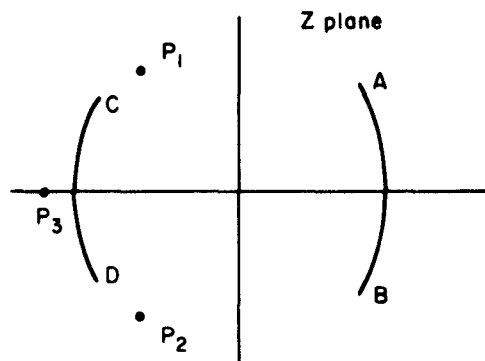$$(18) \qquad \tilde{\chi}(z) = \lim_{V \to \infty} \chi(V, z)$$

Figure 3

will in this case be completely defined along the positive real axis, but it will consist of *two* analytic pieces, one inside the arc AB of zero's and one outside.   From the theory of single charge layers one knows that at the crossing point z_c these two pieces will be continuous but the first derivative will have a discontinuity.

Clearly for any finite but large V, the argument given in Chapter II to obtain from (15) the free energy and hence the pressure is still valid, so that the isotherm is determined by the generalized Mayer equations:

$$\frac{1}{v} = z_0 \frac{\partial \bar{\chi}(z_0)}{\partial z_0},$$

(19)

$$\frac{p}{kT} = \bar{\chi}(z_0)$$

involving now the limit function $\bar{\chi}(z)$.   Because of the discontinuity in the first derivative of $\bar{\chi}$ along the positive real axis, the functions $z \, d\bar{\chi}/dz$ and $\bar{\chi}(z)$ will look about as shown in Figs. 4 and 5.   The isotherm which follows by eliminating the saddle point will therefore have the desired form (Fig. 6).   Let me conclude with the following remarks:

(a) The curves $z \, d\bar{\chi}/dz$ and $\bar{\chi}(z)$ are the limit curves of a series of functions $z \, \partial \chi(V, z)/\partial z$ and $\chi(V, z)$ which are analytic along the real axis.   How one of these functions might approximate the limit curve is indicated by the dotted lines.   It shows again that the condensation phenomenon is a *limit* property.

(b) Of course these considerations of Yang and Lee are not a complete theory of the condensation phenomenon.   They show only
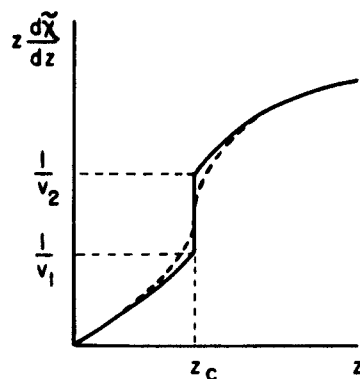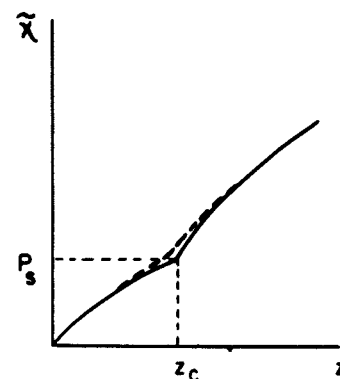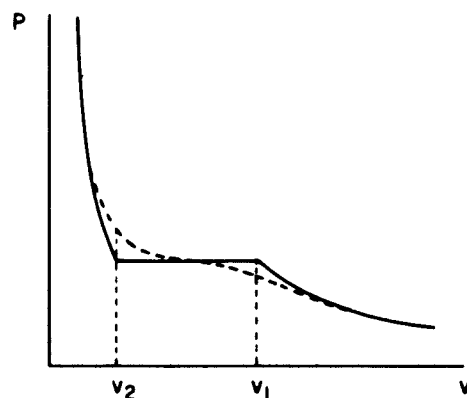
Figure 4

Figure 5

Figure 6

a possible (and I think very likely) *mathematical* "mechanism", and they show how subtle and difficult the real theory will be.

(c) If the Yang-Lee picture is correct then the Mayer limit function $\bar{\chi}(z)$ discussed in Chapter II will have a non-zero radius of convergence and it will be identical to the inner part of $\bar{\chi}(z)$ for a region around the origin. But this $\bar{\chi}(z)$ or even its analytic continuation will *not* determine the condensation point, since the outer part of $\bar{\chi}(z)$ is *not* determined by the inner part of $\bar{\chi}(z)$.

(d) The role which the hard core assumption for the intermolecular force plays in the argument may seem quite striking, and one might

even think that therefore a gas of hard spheres will also show the condensation phenomenon. This is of course *not* necessarily so. The charges may concentrate in single layers, but if for $V \to \infty$ the charges do not close down on the real axis, that is to say if there is always a gap, then there will be *no* condensation since $\tilde{\chi}(z)$ will then be analytic along the whole real axis.

4. Some examples.[4] To make things more concrete, we consider here a few artificial examples constructed to illustrate the analytic features of the theory. Unfortunately, no one has ever been able to compute the partition function for a realistic model of a gas, so our examples must be quite ad hoc.

Suppose that the grand canonical ensemble partition function has the form:

$$(20) \qquad Z_{gr}(V, z) = (1 + z)^V \frac{1 - z^V}{1 - z},$$

where we take V to be an integer. Here V is, say, the volume measured in units r_0^3 and is analogous to the M in Eq. (16). The canonical ensemble partition function corresponding to (20) is obtained by expanding in powers of z and identifying $Z(V, N)$ as the coefficient of z^N. We find:

$$(21) \qquad Z(V,N) = \sum_{N_0 = 0}^{V} \binom{V}{N - N_0}.$$

This model has been constructed so that it has the general features which the partition function of a real gas must have, i.e. the function $Z_{gr}(V, z)$ is a polynomial of degree $2V$ with positive coefficients and the coefficients are monotonically increasing functions of V for fixed N. In our example (20) the $2V$ zeros of Z_{gr} are all on the unit circle, half of them at $z = -1$, the other half at the Vth roots of unity other than $z = -1$. There are no real positive zeros. It is now easy to show that for this model the limit function $\tilde{\chi}(z)$ is given by:

$$(22) \qquad \tilde{\chi}(z) = \begin{cases} \ln(1 + z), & \text{for } z < 1, \\ \ln(1 + z) + \ln z, & \text{for } z > 1. \end{cases}$$

This is just the logarithmic potential due to one unit of charge at $z = -1$ and one unit of charge distributed in a uniform single layer on the unit circle. The function $\tilde{\chi}(z)$ is continuous along the positive real axis but its derivative has a discontinuity at $z = 1$. Note that $\tilde{\chi}(z)$ outside the unit circle is not the analytic continuation of $\tilde{\chi}(z)$

inside the circle. Also note that the function $\bar{\chi}(z)$ introduced in §6, Ch. II is just:

$$(23) \qquad \bar{\chi}(z) = \ln(1 + z).$$

This function has no singularities along the positive real axis, indeed its only singularities are logarithmic branchpoints at $z = -1$ and $z = \infty$.

The equation of state corresponding to (22) is readily obtained using the Mayer equations (19). We find

$$(24) \qquad \frac{p}{kT} = \begin{cases} \ln \dfrac{v}{v-1} = \dfrac{1}{v} + \dfrac{1}{2v^2} + \dfrac{1}{3v^3} + \cdots, & v > 2, \\[2mm] \ln 2 & , \quad 2 > v > \dfrac{2}{3}, \\[2mm] \ln \dfrac{v(1-v)}{(2v-1)^2} & , \quad \dfrac{2}{3} > v > \dfrac{1}{2}. \end{cases}$$

This is the typical form of the isotherm for a condensing gas. Note that the virial expansion of the equation of state is convergent for $v > 1$ while the gas condenses at $v = 2$. Hence, an important thing we learn from this model is that we cannot in general determine the point of condensation or the properties of the condensed phase from a study of the equation of state in the gas phase alone, i.e. from the virial series.

Note that one can obtain the equation of state also *directly* by computing the limit:

$$-\frac{1}{kT}\psi(v) = \lim_{N \to \infty} \frac{1}{N} \ln Z(Nv, N)$$

using (21) for $Z(V, N)$. One does not *need* to introduce the grand canonical partition function, although of course it is quite a good trick!

It may still be of interest to consider a wider class of models, namely those in which the zeros of Z_{gr} all lie on the unit circle. If we introduce $g(\theta)$ such that $Vg(\theta)\, d\theta$ is the number of zeros of Z_{gr} which lie between θ and $\theta + d\theta$ on the unit circle, then the limit function $\bar{\chi}(z)$ will be the logarithmic potential due to a charge distribution with density $g(\theta)$ on the unit circle, so that:

$$(25) \qquad \bar{\chi}(z) = \int_{-\pi}^{+\pi} d\theta\, g(\theta) \ln(1 - ze^{-i\theta}).$$

Since Z_{gr} is a real function its zeros must be distributed symmetrically with respect to the real axis, i.e.

(26)
$$g(\theta) = g(-\theta),$$

We can find further properties of $g(\theta)$ by expanding both sides of (25) in powers of z for $|z| < 1$. Since for $|z| < 1$:

(27)
$$\tilde{\chi}(z) = \bar{\chi}(z) = \sum_{l=1}^{\infty} b_l z^l,$$

one finds:

(28)
$$b_l = -\frac{1}{l} \int_{-\pi}^{+\pi} d\theta \, g(\theta) \cos l\theta.$$

Thus, the b_l's are directly related to the coefficients in the Fourier cosine series expansion of $g(\theta)$. Hence we can write:

(29)
$$g(\theta) = \frac{1}{2\pi} g_0 - \frac{1}{\pi} \sum_{l=1}^{\infty} l b_l \cos l\theta.$$

Here,

(30)
$$g_0 = \int_{-\pi}^{\pi} d\theta \, g(\theta)$$

is the total charge in the distribution. From (29) we see explicitly that $g(\theta)$ cannot be completely determined from a knowledge of the b_l's, i.e. from $\bar{\chi}(z)$; there is still the undetermined constant g_0. From (25) one can readily show that in general:

(31)
$$\chi(z) = \chi\left(\frac{1}{z}\right) + g_0 \ln z.$$

Hence, we can write

(32)
$$\tilde{\chi}(z) = \begin{cases} \bar{\chi}(z), & |z| < 1, \\ \bar{\chi}\left(\frac{1}{z}\right) + g_0 \ln z, & |z| > 1. \end{cases}$$

Here we see explicitly that $\tilde{\chi}$ in the outer region cannot in general be determined from $\tilde{\chi}$ in the inner region.

1. L. Van Hove, Physica **15** (1949) 951. We follow the presentation given by R. J. Riddell in his dissertation (*Contributions to the Theory of Condensation*, University of Michigan, 1951).

2. This proof should be compared with the proof given by C. N. Yang and T. D. Lee, Phys. Rev. **87** (1952) 404, Appendix I. With the same assumptions for the intermolecular potential and using essentially the same method as Van Hove, Yang and Lee prove that the limit:

(a)
$$\check{\chi}(T, z) = \lim_{V \to \infty} \frac{1}{V} \ln Z_{\text{gr}}(V, T, z)$$

exists. In addition they prove that both $\check{\chi}(z)$ and $z \, \partial \check{\chi}/\partial z$ for positive real z are monotonically increasing with increasing z and that $\check{\chi}(z)$ must be continuous.

Since the grand partition function Z_{gr} is a polynomial with positive coefficients from which for large N the partition function $Z(Nv, T, N)$ follows by the steepest descent method (see Chapter II, §7) it is clear that from the existence of the limit (a) and from the properties of $\check{\chi}$ and $z \, \partial \check{\chi}/\partial z$ *both* parts of the Van Hove theorem follow. The question arises whether the inverse of this statement is also true. Can one deduce from the Van Hove theorem the existence of the limit (a) and the properties of $\check{\chi}(z)$. This is of course very likely but a formal proof (which we owe to M. Kac) is perhaps not superfluous.

Let us assume that with increasing volume the vessel always keeps the same shape. One then can introduce a Laplace transform of Z_{gr} by:

(b)
$$\int_0^\infty dV \, e^{-sV} Z_{\text{gr}}(V, T, z) = \sum_{N=0}^\infty z^N \int_0^\infty dV \, e^{-sV} Z(V, T, N)$$
$$= \frac{1}{s} + \sum_{N=1}^\infty N z^N \int_0^\infty dv \, e^{-Nsv} Z(Nv, N)$$

putting $V = Nv$ and omitting from now on the variable T. Since for fixed N, $Z(Nv, N) \sim v^N$ for large v (ideal gas limit) the integral in (b) for $s > 0$ always converges, and one can conclude that the abscissa of convergence of the Laplace integral is determined by the convergence

of the series over N. According to the first part of the Van Hove theorem $Z(Nv, N) \cong \exp(-N\beta\psi(v))$ if N is large. Using the method of steepest descent the integral in (b) can therefore for large N be approximated by:

(c) $\qquad \int_0^\infty dv\, e^{-N[sv + \beta\psi(v)]} \cong \left(\frac{2\pi}{N\psi''(v_0)}\right)^{1/2} e^{-N[sv_0 + \beta\psi(v_0)]}$

where the saddle point v_0 is determined by

(d) $\qquad\qquad s + \beta\dfrac{\partial\psi(v_0)}{\partial v_0} = 0.$

Here we also have used the fact that for $v > 0$ $\partial\psi/\partial v < 0$ and $\psi'' \equiv \partial^2\psi/\partial v^2 > 0$ which follows from the second part of the Van Hove theorem and from the fact that the pressure $p = -\partial\psi/\partial v$ is always positive, since it is positive in the ideal gas limit.

From (b) and (c) one concludes that the abscissa of convergence of the Laplace integral is that positive value of $s = \tilde\chi$ for which:

(e) $\qquad\qquad ze^{-[\tilde\chi v_0 + \beta\psi(v_0)]} = 1$

where v_0 is determined from (d) which we now write as:

(f) $\qquad\qquad \tilde\chi = -\beta\dfrac{\partial\psi(v_0)}{\partial v_0}.$

Eqs. (e) and (f) are two simultaneous equations from which $\tilde\chi$ and v_0 are to be determined as functions of z. We shall show from the Van Hove theorem that there is always an unique solution for $\tilde\chi$, which implies that for large V:

$$Z_{gr}(V, z) \cong e^{V\tilde\chi(z)}$$

so that the Yang-Lee limit (a) exists. The properties of $\tilde\chi(z)$ also follow from (e) and (f). To see all this, write Eq. (e) in the form:

(g) $\qquad\qquad \psi(v_0) - v_0\dfrac{\partial\psi(v_0)}{\partial v_0} = \dfrac{1}{\beta}\ln z$

using (f). This is now an equation for v_0 as function of z, and then (f) determines $\tilde\chi$. Eq. (g) can most easily be discussed graphically. Suppose first that no condensation occurs. Then according to Van Hove $\psi(v)$ is a monotonic decreasing and upward concave function of v. For any value of z, v_0 is then uniquely determined by drawing

the tangent from the point $(\ln z)/\beta$ on the ψ-axis (see Fig. a) and the slope of the tangent determines $\bar{\chi}$ according to (f).

Next suppose that there is a condensation region, which of course the Van Hove theorem does not exclude. Then the $\psi(v)$ curve will have a straight part with a slope corresponding to the saturated vapour pressure (see Fig. b). Clearly in this case the tangent construction gives for $z < z_c$ a value for $v_0 > v_2$, for $z > z_c$ a value for $v_0 < v_1$, while for $z = z_c$ v_0 is not uniquely determined. However,
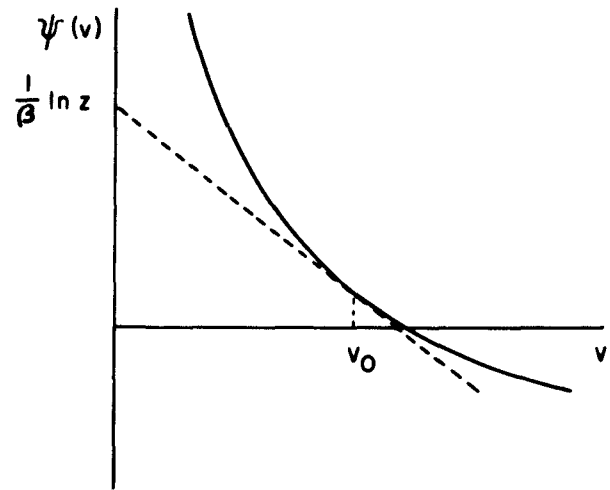

Figure a

the slope of the tangent and therefore $\bar{\chi}$ is for any z uniquely fixed, and one easily sees that $\bar{\chi}$ is a continuous and monotonically increasing function of z. Finally, since by differentiation after z, one deduces from (f) and (g) that:

$$\frac{1}{v_0} = z \frac{\partial \bar{\chi}}{\partial z}$$

and since v_0 is a monotonically decreasing function of z which has a discontinuity in the case condensation occurs, it is clear that $\bar{\chi}(z)$ has all the Yang-Lee properties.

It should be emphasized that in this equivalence proof *both* parts of the Van Hove theorem have been used. The existence of the limit:

(i)
$$-\beta\psi(v) = \lim_{N\to\infty} \frac{1}{N} \ln Z(Nv, N)$$

is *not* enough.   For instance for the van der Waals' expression for Z:

(j)
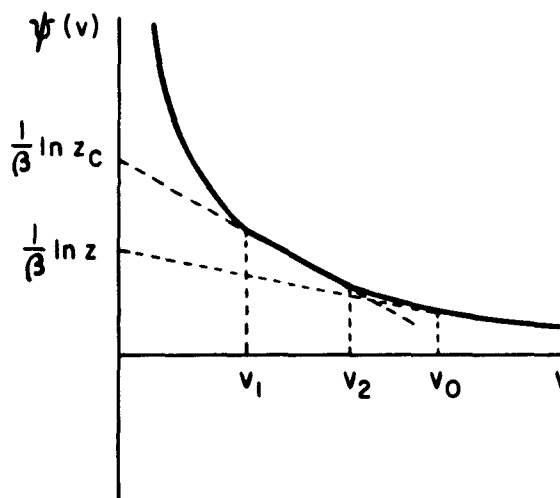$$Z = \frac{1}{N!\lambda^{3N}} (V - Nb)^N \exp\left[\frac{\beta a}{V} N(N - 1)\right]$$

Figure b

the limit (i) exists, but

(k)
$$p = -\frac{\partial\psi}{\partial v} = \frac{kT}{v - b} - \frac{a}{v^2}$$

is not monotonic.   Constructing from (j) the grand canonical partition function, it is then not difficult to show that this leads to the van der Waals equation (k) plus the Maxwell rule in the condensation region.

3. C. N. Yang and T. D. Lee, *Statistical Theory of Equations of State and Phase Transitions.* I. *Theory of Condensation;* Phys. Rev. **87** (1952) 404.   In the following paper: *Lattice Gas and Ising Model*, Phys. Rev. **87** (1952) 410 the same authors apply their general theory to a so-called lattice gas, in which one assumes that the molecules of the gas are restrained to lie on the lattice points of a cubical lattice. Each lattice point is either vacant or occupied but no two molecules can be on the same site.   Assuming in addition that only nearest neighbours attract each other, the authors show that the zeros of the

grand partition function all lie on a circle, and that in two dimensions condensation occurs.

4. The first example (Eq. (20)) is due to G. W. Ford. Lee and Yang (l.c. Note 3, p. 415) introduced the density distribution $g(\theta)$ of the zeros on the unit circle which leads to Eq. (25) and also Eq. (28) for the b_l is due to them.

The Boltzmann Equation

1. Introduction. We now will begin with the discussion of the non-equilibrium properties of gases, that is we return to the basic problem of Boltzmann: why and how is the equilibrium state reached in time. Following the historical development, I will start with the theory of dilute gases according to the so-called kinetic method of Boltzmann, and will discuss later how this may fit into the general Boltzmann-Gibbs picture of the approach to equilibrium which was sketched in the first chapter.

The basic equation of the kinetic method is the famous Boltzmann equation:[1]

$$(1) \qquad \frac{\partial f}{\partial t} = -\,\mathbf{v}\cdot\frac{\partial f}{\partial \mathbf{r}} - \mathbf{a}\cdot\frac{\partial f}{\partial \mathbf{v}} + \int d\mathbf{v}_1 \int d\Omega\, g I(g, \theta)(f'f'_1 - f f_1)$$

which expresses how the number of molecules

$$f(\mathbf{r}, \mathbf{v}, t)\, d\mathbf{r}\, d\mathbf{v}$$

in the element $d\mathbf{r}\, d\mathbf{v}$ of the six dimensional phase space (μ-space) of a molecule changes in time due to the streaming in μ-space and due to the collisions with other molecules. In (1) $\mathbf{a}$ is the acceleration due to an *outside* potential $U(r)$ and the streaming part of (1):

$$(2) \qquad S(f) \equiv -\,\mathbf{v}\cdot\frac{\partial f}{\partial \mathbf{r}} - \mathbf{a}\cdot\frac{\partial f}{\partial \mathbf{v}}$$

is clearly just the local change of f per second due to the independent motion of the molecules in μ-space. One can also say, that $S(f)$ is the one particle Liouville operation $\{H, f\}$ with $H = (p^2/2m) + U(r)$. The last term in (1) describes the effect of the collisions; here the prime and the index 1 of the f's refer to the velocity variable only, so that for instance $f_1 \equiv f(\mathbf{r}, \mathbf{v}_1, t)$ and the four velocity variables refer to the velocities of the binary collision $(\mathbf{v}, \mathbf{v}_1) \rightleftarrows (\mathbf{v}', \mathbf{v}'_1)$; $g = |\mathbf{v} - \mathbf{v}_1| = |\mathbf{v}'_1 - \mathbf{v}'|$ is the relative velocity which in a collision turns over the angle θ. To find the number per c.c. and per second of the *direct*

collisions $(v, v_1) \rightarrow (v', v_1')$, Boltzmann argues as follows (see Fig. 1). Consider the relative motion and surround all molecules with velocity v with an action sphere with a radius equal to the range of the forces. All molecules with velocity between v_1 and $v_1 + dv_1$, which enter the action sphere with a *collision parameter* between p and $p + dp$ and which lie in the little cylinder $gp\, dp\, d\varepsilon\, dt$ (ε is a polar angle) will in the
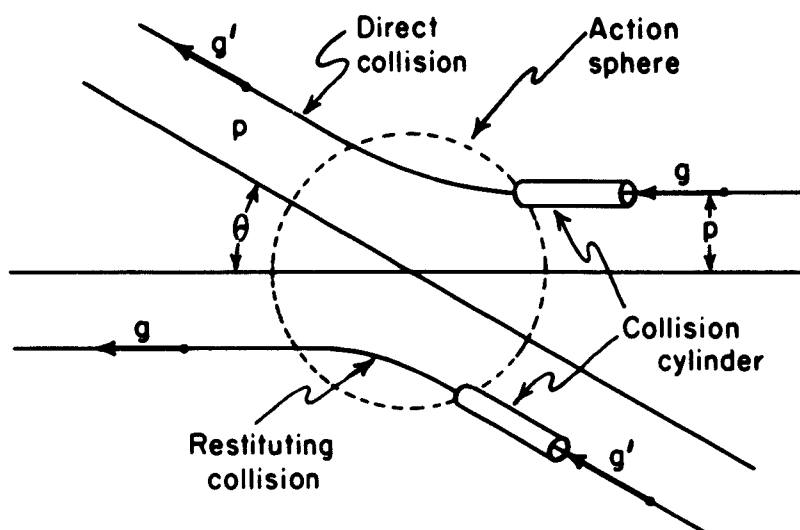

Figure 1

next time element dt collide with a molecule of velocity v and in this collision g will turn over an angle θ. The relation between p, g and θ is determined by the dynamics of the collision; in fact:

$$(3) \qquad \theta = \pi - 2 \int_0^{\eta_0} \frac{d\eta}{\left[1 - \eta^2 - \frac{2}{mg^2}\phi\left(\frac{p}{\eta}\right)\right]^{1/2}}$$

where η_0 is the smallest root of the expression under the radical sign. Now, since there are $f\, dv$ molecules with velocity v per c.c., and since each molecule with this velocity carries a collision cylinder, Boltzmann puts for the number of direct collisions per c.c. and per second:

$$(4) \qquad \begin{aligned} dA &= gp\, dp\, d\varepsilon\, ff_1\, dv\, dv_1 \\ &= gI(g, \theta)\, d\Omega\, ff_1\, dv\, dv_1 \end{aligned}$$

where we have written:

$$p \, dp \, d\varepsilon = I(g, \theta) \, d\Omega.$$

$I(g, \theta)$ is called the differential collision cross-section for a collision into the solid angle $d\Omega = \sin \theta \, d\theta \, d\varepsilon$. Clearly $I(g, \theta)$ through (3) is uniquely determined by the force law $\phi(r)$.

Similarly Boltzmann puts for the number of *restituting* collisions $(v', v_1') \rightarrow (v_1, v_2)$ per c.c. and per second:

$$(5) \qquad\qquad dB = gI(g, \theta) \, d\Omega f'f_1' \, dv' \, dv_1'.$$

Since the transformation from v, v_1 to v', v_1' as determined by the conservation laws of energy and momentum, is clearly a linear orthogonal transformation, $dv \, dv_1 = dv' \, dv_1'$, and from (4) and (5) one obtains therefore the collision term in the Boltzmann equation (1) since each direct collision is a *loss* and each restituting collision a *gain* in the number of molecules $f \, dv$ under consideration.

Eqs. (4) and (5) express the so-called *Stosszahl-Ansatz*, which may seem intuitively quite evident, but which is of course an assumption of a non-mechanical nature. I will postpone the critical discussion of this assumption to Chapter VII. For the time being let us accept that the Boltzmann equation describes how the distribution function $f(r, v, t)$ of the molecules in μ-space changes in time.

2. The approach to equilibrium. Since (1) is of the first order in the time, a basic problem is the initial value problem: given the distribution function $f(r, v, 0)$ at $t = 0$, find the distribution at any later time. It was a great triumph for Boltzmann that he was able to show that *any* initial distribution approaches in the course of time the Maxwell-Boltzmann distribution:

$$(6) \qquad\qquad f_0 = A_0 \exp\left[-\beta\left\{\frac{mv^2}{2} + U(r)\right\}\right]$$

for sufficiently general outside potentials $U(r)$. In here A_0 and β are constants which are determined by the given total number and total energy of the molecules.

Since Boltzmann's arguments are so well known, I will only sketch his proof.

The first step is the famous *H-theorem*. Let

$$(7) \qquad\qquad H(t) = \int \int f \log f \, dr \, dv;$$

then:

$$\frac{dH}{dt} = \int \int \frac{\partial f}{\partial t} \log f \, d\mathbf{r} \, d\mathbf{v} = \left(\frac{dH}{dt}\right)_{\text{streaming}} + \left(\frac{dH}{dt}\right)_{\text{collisions}}$$

using (1) for $\partial f / \partial t$. Due to the streaming the H function does *not* change. This follows from the Liouville theorem. As mentioned already in Chapter I, §2, the integral over the whole phase space of any function $F(\rho)$ of the density of the ensemble fluid will be independent of the time. Since with independent molecules the gas *is* an ensemble of which the density is f, one can conclude that the integral of $f \log f$ over the phase space ($= \mu$-space) will not change with time because of the streaming. Due to the collisions H *always* decreases since by a few simple and classical transformations one can write:[2]

$$\left(\frac{dH}{dt}\right)_{\text{coll.}} = \frac{1}{4} \int d\mathbf{v} \int d\mathbf{v}_1 \int d\Omega \, gI(g, \theta)(f'f_1' - ff_1) \ln \frac{ff_1}{f'f_1'} \le 0,$$

dH/dt is zero *only* if for all possible collisions

$$(8) \qquad\qquad ff_1 = f'f_1'$$

and this state will be reached monotonically in time. Eq. (8) determines the dependence of the equilibrium distribution on the velocities. In fact the only solution of the functional equation (8) is:

$$(9) \qquad\qquad f = A \exp\left\{ -\frac{\beta m}{2}(\mathbf{v} - \mathbf{u})^2 \right\}$$

where A, β and the average velocity $\mathbf{u}$ can still be functions of $\mathbf{r}$ *and* t. From the Boltzmann equation follows that an f of the form (9) must still fulfill the equation:

$$(10) \qquad\qquad \frac{\partial f}{\partial t} + \mathbf{v} \cdot \frac{\partial f}{\partial \mathbf{r}} + \mathbf{a} \cdot \frac{\partial f}{\partial \mathbf{v}} = 0$$

and one can show that for a sufficiently general outside potential $U(\mathbf{r})$ (which include the shape of the vessel or of the wall potential), the *only* solution of (10) which is of the form (9) is found by putting in (9) $\mathbf{u} = 0$, β equal to a constant independent of $\mathbf{r}$ and t, and:

$$(11) \qquad\qquad A = A_0 e^{-\beta U(\mathbf{r})}$$

where A_0 is a constant.

The proof is given in Note 3. Let me only say that for special outside potentials for instance a harmonic potential $U(\mathbf{r}) = \omega r^2/2$, the spatial equilibrium distribution (11) will *not* be reached in time. For such special potentials there are a host of special solutions of the

Boltzmann equation, in which the dependence on the velocity always has the form (9) but where the A, β and u can be functions of space and time. Boltzmann himself gave a detailed discussion of these solutions (see Boltzmann, Wissenschaftliche Abhandlungen, Vol. II, p. 83). They have however only a limited interest.

Let me conclude with a number of remarks.

(a) Clearly Boltzmann does not actually solve the initial value problem stated in the beginning of this section. In fact he supposes in the first place that the initial value problem has an unique solution and then that if at $t = 0$ the distribution function f goes to zero for r, $v \to \infty$ sufficiently fast for the convergence of all the required integrals (especially for the total number, for the total energy and for H), then also for any later time these integrals remain convergent. From the mathematical point of view the proof of Boltzmann is therefore not irreproachable. For the spatially uniform case ($U \equiv 0$; f only function of v and t) and for elastic spheres ($I(g, \theta)$ = constant) Carleman has given a rigorous proof.[4] I will not try to indicate the method Carleman uses, since it does not add to the physical insight. I do think though that an extension of Carleman's work especially to the spatially non-uniform case would be quite valuable.

(b) The proof of Boltzmann does *not* mean, that the approach to equilibrium happens in two sharply separated successive stages: first the approach in velocity space to the Maxwell distribution (9) and then the approach in coordinate space to the "barometric" distribution (11). Both approaches are coupled to each other and the velocity distribution will be strictly Maxwellian *only* if the complete equilibrium is reached.

(c) However it *is* true that the approach to equilibrium in velocity space is quite different from the approach to equilibrium in coordinate space. It is physically plausible and it is also suggested by Boltzmann's proof, that the velocity distribution in any volume element of space will approach a *local* Maxwell distribution of the form (9) very quickly and in a monotonic fashion. It will never reach it because the streaming and the outside forces will interfere, but it will have this tendency. On the other hand the approach to equilibrium in coordinate space is not monotonic in general and will require a much longer time. Of course this picture of the approach to the complete Maxwell-Boltzmann distribution (6) must and can be confirmed by a deeper study of the Boltzmann equation. It is the basis of a successive approximation method (the Chapman-Enskog development) which we will discuss in Chapter VI.

3. The linearized Boltzmann equation. Accepting the fact that the Maxwell-Boltzmann distribution (6) will be reached in time it is clearly of interest to investigate the case of a small disturbance of the equilibrium state.   Put in (1):

$$(12) \qquad f = f_0[1 + h(\mathbf{r}, \mathbf{v}, t)]$$

and neglect the quadratic terms in h.   One then gets the linearized Boltzmann equation:

$$\frac{\partial h}{\partial t} = -\mathbf{v} \cdot \frac{\partial h}{\partial \mathbf{r}} - \mathbf{a} \cdot \frac{\partial h}{\partial \mathbf{v}} + \int d\mathbf{v}_1 \int d\Omega\, gI(g, \theta) f_{01}(h' + h'_1 - h - h_1)$$

$$(13)$$

$$= S(h) + C(h).$$

Consider first the spatial uniform case, in which there are no external forces, so that the disturbance h depends only on $\mathbf{v}$ and t, and

$$(14) \qquad f_0 = n\left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{mv^2}{2kT}\right)$$

where the number density n and the temperature T are constants. To solve the initial value problem, it is clearly of interest to find the eigenfunctions ψ_i and eigenvalues λ_i of the collision operator C, defined by

$$(15) \qquad C(\psi_i) = \lambda_i \psi_i.$$

Some properties are quite obvious.

(a) There are five zero eigenvalues corresponding to the eigenfunctions 1, $\mathbf{v}$, v^2; this is a consequence of the five conservation laws during a collision.

(b) All other eigenvalues must be *negative*.

PROOF.

$$\lambda_i = \frac{\int d\mathbf{v}\, f_0 \psi_i C(\psi_i)}{\int d\mathbf{v}\, f_0 \psi_i^2}$$

and:

$$\int d\mathbf{v}\, f_0 \psi_i C(\psi_i) = -\frac{1}{4} \int d\mathbf{v} \int d\mathbf{v}_1 \int d\Omega\, gI(g, \theta) f_0 f_{01}(\psi'_i + \psi'_{i1} - \psi_i - \psi_{i1})^2$$

using the same transformations as used in the proof of the H-theorem.

(c) Different eigenfunctions are orthogonal to each other.   This follows from:

$$\int d\mathbf{v}\, f_0 \psi_i C(\psi_j) = \int d\mathbf{v}\, f_0 \psi_j C(\psi_i).$$

(d) The operator C is an isotropic operator in velocity space and therefore the eigenfunctions will have the form:

$$(16) \qquad \psi_{rlm} = R_{rl}(v)\, Y_{lm}(\theta, \phi)$$

using polar coordinates in velocity space, and the eigenvalues λ_{rl} will at least be $(2l + 1)$-fold degenerate.

Assuming that the ψ_i form a complete set, one can clearly solve the initial value problem in the spatially uniform case by developing $h(v, t)$ in the ψ_i and one gets:

$$(17) \qquad h(v, t) = \sum_i c_i e^{\lambda_i t}\psi_i(v)$$

where the c_i are determined from $h(v, 0)$. Since $\lambda_i \leqq 0$, (17) shows that h goes to zero except for the permanent changes in density, average velocity and temperature. The quantities $1/\lambda_i$ clearly represent a *spectrum of relaxation times*.

The question remains, whether such a *discrete* spectrum of relaxation times really exists. So far as I know this has *not* been proved in general. One does know[5] that the collision operator $C(h)$ is of the form:

$$(18) \qquad C(h) = -\sigma(v)h + \int dv_1 f_{01} K(v, v_1) h(v_1)$$

but the kernel $K(v, v_1)$ is singular, so that the usual theory is not applicable. It is still simple to see that whatever the spectrum is, it is bounded from below, if:

$$\int dv f_0 \sigma(v) = \int dv \int dv_1 f_0 f_{01} \int d\Omega g I(g, \theta)$$

exists, which implies that the total cross section:

$$(19) \qquad Q(g) = \int d\Omega\, I(g, \theta)$$

must be *finite*, which again follows from the physically natural assumption that the forces have a finite range. I believe that, in this case, the spectrum will be discrete and that the λ_i will approach a finite negative limit point. But even for hard spheres ($I(g, \theta) = $ const.) this has not been proved.[6]

Because of these uncertainties, it is reassuring that for *one* special case the spectrum and the eigenfunctions can be determined explicitly. Since for this case we will discuss in the next chapter a special application of the linearized Boltzmann equation, I will collect here the precise formula.

Going back to (13), introduce dimensionless velocity variables by putting:

$$c = \left(\frac{m}{2kT}\right)^{1/2} v$$

and similarly for v_1. Put also:

$$\tau = \left(\frac{2kT}{m}\right)^{1/2} t$$

then with $a = 0$ (no outside fields), so that f_0 is still given by (14), the linearized Boltzmann equation becomes:

$$(20) \qquad \frac{\partial h}{\partial \tau} + c \cdot \frac{\partial h}{\partial r} = n\sigma J(h)$$

with:

$$(21) \qquad J(h) = \frac{1}{\pi^{3/2}} \int dc_1 \exp(-c_1^2) \int d\Omega \, F(g, \theta)[h' + h_1' - h - h_1],$$

$$(22) \quad F(g, \theta) = \left(\frac{m}{2kT}\right)^{1/2} g \frac{I(g, \theta)}{\sigma}.$$

σ is a constant of the order of the total cross section, which is introduced to make $F(g, \theta)$ dimensionless. I will call $J(h)$ the dimensionless collision operator. It still has of course the same properties as $C(h)$.

Now *assume* that $F(g, \theta)$ is a function of θ alone. Since the relation between the velocities c', c_1' after collision and the velocities c, c_1 before collision is a *linear* relation, it is clear that in this case if h is a polynomial of degree n in v also $J(h)$ will be a polynomial of degree n in v. The eigenfunctions of J will therefore be polynomia, and in fact one can verify that the eigenfunctions, written again in polar coordinates in velocity space, are:

$$(23) \qquad\qquad \psi_{rlm} = N_{rlm} S_{l+1/2}^{(r)}(c^2) c^l Y_{lm}(\theta, \phi)$$

where the $S_{l+1/2}^{(r)}$ are the associated Laguerre polynomia (also called Sonine polynomia). $S_n^{(m)}(x)$ is defined as the coefficient of t^m in

$$(1 - t)^{-n-1} \exp\left\{-\frac{xt}{1-t}\right\}$$

and their explicit expression is:

$$S_n^{(m)}(x) = \sum_{p=0}^{m} (-x)^p \frac{(n+m)!}{p!(m-p)!(n+p)!}.$$

In (23) the N_{rlm} are normalization constants. The $\psi_{rlm}(c)$ form a complete orthogonal set of eigenfunctions with weight function e^{-c^2}, and the corresponding eigenvalues are:

$$
\lambda_{rl} = 2\pi \int_0^\pi d\theta \sin \theta F(\theta) \left[\cos^{2r+l} \frac{\theta}{2} P_l\left(\cos \frac{\theta}{2}\right) \right.
$$
$$
\left. + \sin^{2r+l} \frac{\theta}{2} P_l\left(\sin \frac{\theta}{2}\right) - 1 - \delta_{r0}\,\delta_{l0} \right].
$$

(24)

Eqs. (23) and (24) were found first by C. S. Wang Chang and then also independently by L. Waldmann.[7] Note that the five zero eigenvalues are λ_{00}, λ_{01} and λ_{10} corresponding to the eigenfunctions 1, c and $(3/2 - c^2)$. One further sees from (24) that the λ_{rl} converge for large r and l to:

$$
(25) \qquad\qquad -2\pi \int_0^\pi d\theta \sin \theta F(\theta)
$$

which we can assume to be equal to -1 by the proper choice of σ.

I will call this special case of the linearized Boltzmann equation the *quasi-Maxwell model*. It is *not* a realistic model, in the sense that there is no intermolecular potential for which $F(g, \theta)$ depends only on θ *and* for which the integral (25) converges. When the force is equal to κr^{-5} (*Maxwell model*),

$$
gI(g, \theta) = \left(\frac{2\kappa}{m}\right)^{1/2} F_M(\theta)
$$

but for small θ, $F_M(\theta) \sim \theta^{-5/2}$ so that (25) diverges, corresponding to the fact that $\phi(r)$ has an infinite range.[8] However, it seems to me that the quasi-Maxwell model must be quite similar to the actual case of forces with finite range, and will give therefore at least a qualitative insight.

Finally let me point out, that in (19) the order of magnitude of the eigenvalues of the collision operator $n\sigma J(h)$ is clearly $n\sigma$, which corresponds to the order of magnitude $n\sigma(kT/m)^{1/2}$ for the eigenvalues λ_i of $C(h)$. Thus $(\lambda_i)^{-1}$ is of the order of the time between collisions which confirms the view that the Maxwell distribution will be reached after a few collisions, that is in a time of the order of the time between collisions.

Notes on Chapter IV

1. For the complete discussion Boltzmann's book *Vorlesungen über Gastheorie* (Ambrosius Barth, Leipzig, 1912) is still indispensable. See esp. Vol. 1, Part II, and Vol. 2, Part VII.

2. One has:

$$\left(\frac{dH}{dt}\right)_{coll} = \int d\mathbf{v} \int d\mathbf{v}_1 \int d\Omega \, g I(g, \theta) \ln f \cdot (f'f_1' - ff_1)$$

$$= \int d\mathbf{v} \int d\mathbf{v}_1 \int d\Omega \, g I(g, \theta) \ln f_1 \cdot (f'f_1' - ff_1),$$

by interchanging $\mathbf{v}$ and $\mathbf{v}_1$. Therefore, adding the two expressions and dividing by two:

$$\left(\frac{dH}{dt}\right)_{coll} = \frac{1}{2} \int d\mathbf{v} \int d\mathbf{v}_1 \int d\Omega \, g I(g, \theta)(f'f_1' - ff_1) \ln (ff_1)$$

$$= \frac{1}{2} \int d\mathbf{v} \int d\mathbf{v}_1 \int d\Omega \, g I(g, \theta)(ff_1 - f'f_1') \ln (f'f_1'),$$

by interchanging the velocities before and after collision and using again $d\mathbf{v} \, d\mathbf{v}_1 = d\mathbf{v}' \, d\mathbf{v}_1'$. Adding the two expressions and dividing by two leads to the form given in the text.

3. Write Eq. (9) in the form:

$$\ln f = -hv^2 + \mathbf{k} \cdot \mathbf{v} + n$$

so that $h = \beta m/2$, $\mathbf{k} = m\beta\mathbf{u}$ and $n = \ln A - \beta m u^2/2$. Substituting in (10) and requiring that (10) must be fulfilled identically in $\mathbf{v}$ leads to the equations:

(a)
$$\frac{\partial h}{\partial x_i} = 0,$$

(b)
$$\frac{\partial k_i}{\partial x_j} + \frac{\partial k_j}{\partial x_i} - 2\frac{\partial h}{\partial t} \delta_{ij} = 0,$$

(c)
$$\frac{\partial k_i}{\partial t} + \frac{\partial n}{\partial x_i} - 2ha_i = 0,$$

(d)
$$\frac{\partial n}{\partial t} + k_\alpha a_\alpha = 0.$$

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From (a) and (b) one concludes that h can only be a function of the time and that

(e) $$\mathbf{k} = \mathbf{k}_0(t) + [\mathbf{\Omega}(t) \times \mathbf{r}] + \frac{dh}{dt}\,\mathbf{r}.$$

At this stage one can say therefore that the average motion of the gas can only be a possibly time dependent combination of a translation, rotation and a radial expansion or contraction. Since $m\mathbf{a} = -\operatorname{grad} U(r)$, it follows from (c) that:

(f) $$\frac{\partial \mathbf{k}}{\partial t} = -\operatorname{grad}\!\left(n + \frac{2h}{m}\,U\right)\!\cdot$$

Therefore the curl of $\partial\mathbf{k}/\partial t$ must be zero, which implies that $\mathbf{\Omega}$ must be a constant and then it follows from (e) and (f) that:

$$n + \frac{2h}{m}\,U = n_0(t) - \frac{d\mathbf{k}_0}{dt}\!\cdot\!\mathbf{r} - \frac{1}{2}\frac{d^2h}{dt^2}\,r^2.$$

Substituting this expression for n in the last equation, (d), which has to be fulfilled, leads to:

(g) $$\frac{1}{m}\,\mathbf{k}\cdot\operatorname{grad} U + \frac{2}{m}\frac{dh}{dt}\,U = \frac{dn_0}{dt} - \frac{d^2k_0}{dt^2}\!\cdot\!\mathbf{r} - \frac{1}{2}\frac{d^3h}{dt^3}\,r^2.$$

Now suppose that from an arbitrary origin the outside potential $U(r)$ can be developed in a power series:

(h) $$U = A_\alpha x_\alpha + \frac{1}{2} A_{\alpha\beta} x_\alpha x_\beta + \frac{1}{6} A_{\alpha\beta\gamma} x_\alpha x_\beta x_\gamma$$

where the A's are known constants. Higher order terms will be neglected since it will turn out that with arbitrary A's the form (h) has already sufficient generality. Introducing (h) in (g), it is clear that only the left hand side will contain terms of the third degree in the x_i. Equating the coefficients of these terms to zero gives ten homogeneous linear equations in the four unknowns dh/dt and $\mathbf{\Omega}$. Thus one finds that in general h must be constant and $\mathbf{\Omega} = 0$. From the terms of the second degree in the x_i, one then can conclude that also $\mathbf{k}_0 = 0$, so that $\mathbf{k}$ is zero all together. From (d) follows, that then n must be independent of the time, and from (c) one concludes that $n + 2hU/m = n_0$ which is equivalent to Eq. (11) in the text.

4. T. Carleman, *Problèmes Mathématiques dans la Théorie Cinétique des Gaz* (Publications Scientifiques de l'Institut Mittag-Leffler, Vol. 2, Uppsala, 1957). The generalization of the proof for other force laws with a finite range is straightforward.

5. This was first shown by D. Enskog, *Kinetische Theorie der Vorgänge in Mässig Verdünnten Gasen*, Dissertation, Uppsala, 1917, p. 140. For a more transparent proof see L. Waldmann, Handbuch der Physik **12**, p. 366.

6. There is also the following troublesome question. Should one impose the condition that the integral:

(i)
$$\int d\mathbf{v}\, f_0 \psi^2$$

exists in order to select the eigenvalues and eigenfunctions of the linear collision operator $C(\psi)$? On the one hand this is necessary if one wants to apply the usual Hilbert space theory. But on the other hand the integral (i) has *no* physical meaning in contrast to the case of the quantum mechanical operators. This difficulty was noticed by N. G. van Kampen (Physica **21** (1955) 949; see especially the remarks on p. 957). L. Waldmann (Handbuch der Physik **12**, p. 365 and p. 367) has tried to connect the square integrability condition with the requirement that the entropy should always exist. However his argument is not convincing.

7. C. S. Wang Chang and G. E. Uhlenbeck: *On the Propagation of Sound in Monatomic Gases*. Report of the Engineering Research Institute, University of Michigan, 1952. L. Waldmann, Handbuch der Physik **12**, §38.

8. Explicitly one finds (see Maxwell, *Collected Papers*, Vol. II, p. 42):

$$F_M(\theta) = \frac{1}{4} \frac{(\cos 2\phi)^{1/2}}{\sin \theta \sin 2\phi \{\cos^2 \phi K(\sin \phi) - \cos 2\phi E(\sin \phi)\}}$$

where ϕ is related to θ by:

$$\frac{\pi - \theta}{2} = (\cos 2\phi)^{1/2} K(\sin \phi).$$

$K(x)$ and $E(x)$ are the complete elliptic integrals of the first and second kind respectively. $F_M(\theta)$ is a monotonic decreasing function of θ; for small θ:

$$F_M(\theta) \cong \frac{(3\pi)^{1/2}}{16} \theta^{-5/2}\left(1 + \frac{35}{24\pi}\theta + \cdots\right)$$

while for $\theta = \pi$:

$$F_M(\pi) = \frac{1}{4K^2(\pi/4)} = 0.0727\cdots.$$

The Propagation of Sound

1. Introduction. As an application of the linearized Boltzmann equation let me consider the propagation of sound in a gas. Clearly, if the gas is in equilibrium and if the intensity of the sound is not too high, then the sound waves will be a small disturbance from equilibrium and should therefore be described by the linearized Boltzmann equation.

First let me tell you some of the experimental facts. . The first question is how fast sound propagates, and the answer seems without mystery and is known to every physics student. He knows that the velocity V_0 depends on the adiabatic compressibility of the gas and that one gets:

$$(1) \qquad V_0 = \left(\frac{c_p}{c_v}\frac{kT}{m}\right)^{1/2} = \left(\frac{5}{3}\frac{kT}{m}\right)^{1/2}$$

for a mono-atomic gas, to which I will always restrict myself. However, if one does not look upon the gas as a macroscopic material with some compressibility, but as a collection of almost independent molecules, then it seems to me that the sound propagation becomes more mysterious. How is it possible to impose on the random motion of the molecules the ordered motion, or in present day terminology the *collective mode of motion*, which a sound wave represents? That one runs into rather deep questions becomes apparent, when one wants to find the frequency dependence of V, the dispersion of sound, and the accompanying absorption of sound. Since the days of Kirchhoff one knows that for increasing frequency, V becomes larger, and absorption sets in. The latter can still be partially understood from the macroscopic point of view. At high frequency the temperature and velocity gradients between compression and rarefaction become so steep that *although* the time between them gets shorter, the heat conduction and the viscosity of the gas begin to have effect and cause absorption. Kirchhoff found for the absorption coefficient in amplitude:

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(2)
$$\alpha_0 = \frac{\omega^2}{\rho V_0^3}\left(\frac{2}{3}\mu + \frac{2}{15}\frac{m\kappa}{k}\right)$$

where ω = angular frequency, ρ the density, μ the viscosity coefficient and κ the heat conduction coefficient of the gas. Note that since $\kappa \sim (k/m)\mu$, $\mu \sim \rho\lambda\langle c\rangle$ with λ the mean free path, $\langle c\rangle$ some average thermal velocity (hence $\langle c\rangle \sim V_0$), (2) shows that $\alpha_0 \sim \lambda/\Lambda^2$ if Λ is the wave length of the sound. Experimentally (2) has been well verified, when the frequency ω is not too high.

What happens if the frequency gets higher and higher? The most extensive experiments have been done by M. Greenspan for helium gas.[1] His method was the usual one, although many precautions and refinements were necessary of course. A piezoelectrically driven quartz plate A produced the sound waves and the density fluctuations were picked up at an identical receiver quartz plate B producing voltage fluctuations which then could be amplified. The difference in phase of the fluctuations between A and B determines the phase velocity and the ratio of the amplitudes gives the absorption coefficient. The distance L between the plates was always *much* larger than the mean free path λ. The results seem to indicate that the velocity V and the absorption coefficient α increase monotonically with frequency. The highest value of λ/Λ which could be realized was of order one and the velocity V had then increased to about $3V_0$, while the absorption coefficient had become of order $1/\lambda$, so that the absorption was tremendous.

What happens for $\omega \rightarrow \infty$? Some people have speculated that V and α might become infinite, since practically infinite velocities occur according to the Maxwell distribution. Others have thought that V might become constant again while the α goes through a maximum, similar to the observed behaviour in poly-atomic gases. But there is no real reason for either belief.

2. The Wang-Chang method. Returning now to the theory, to find the dispersion law of the sound waves it seems natural to seek a solution of the linearized Boltzmann equation (see Chapter IV, §3):

(3)
$$\frac{\partial h}{\partial \tau} + \mathbf{c}\cdot\frac{\partial h}{\partial \mathbf{r}} = n\sigma J(h),$$

$$J(h) = \frac{1}{\pi^{3/2}}\int d\mathbf{c}_1\, e^{-c_1^2}\int d\Omega\, F(g, \theta)[h' + h_1' - h - h_1]$$

which has the form of a plane wave, say in the z-direction. Put therefore:

(4)
$$h = \exp[i(kz - \omega_0\tau)]h_0(\mathbf{c})$$

where $\omega_0 = \omega(m/2kT)^{1/2}$ and $k = 2\pi/\Lambda$ is the wavenumber (not to be confused with the Boltzmann constant k which occurs always in the combination kT). Now develop $h_0(\mathbf{c})$ in the eigenfunctions of $J(h)$:

$$h_0(\mathbf{c}) = \sum_l a_l \psi_l(\mathbf{c}).$$

One clearly gets an infinite set of linear equations

(5)
$$ik \sum_l M_{lm} a_m - i\omega_0 a_l = n\sigma\lambda_l a_l$$

with:

(6)
$$M_{lm} = \int d\mathbf{c} \; c_z \psi_l \psi_m e^{-c^2}.$$

The equations (5) will have a non-trivial solution only if the infinite determinant of the coefficients vanishes. This condition:

(7)
$$\| ik M_{lm} - (i\omega_0 + n\sigma\lambda_l)\delta_{lm} \| = 0$$

gives a relation between ω_0 and k and hence expresses the dispersion law of the gas. However, the discussion is hard. All that we could think of was to break off the determinant successively. It is simple to see that taking only the first three rows and columns, corresponding to the three zero eigenvalues (for which the eigenfunctions are 1, c_z and $c^2 - 3/2$, so that the corresponding elements of M_{lm} are simple to evaluate), leads to the cubic equation:

$$\omega_0\left(\omega_0^2 - \frac{5}{6}k^2\right) = 0$$

with the three roots $\omega_0 = 0$, $\omega_0 = \pm k(5/6)^{1/2}$. The last two roots clearly represent "propagating" modes going to the right and left with the velocity:

$$V_0 = \frac{\omega}{k} = \frac{\omega_0}{k}\left(\frac{2kT}{m}\right)^{1/2} = \left(\frac{5}{3}\frac{kT}{m}\right)^{1/2}$$

so that we have derived Eq. (1). By taking more rows and columns one gets higher order algebraic equations in ω_0, and by then following the propagating modes (that is the roots which for $k \to 0$, become $\pm k(5/6)^{1/2}$) one can see what happens for larger k or smaller wavelengths. This is straightforward for the quasi-Maxwell model, and

one obtains series expansions for the velocity V and the absorption coefficient α of the form:

(8)

$$V = V_0\left[1 + a_1\left(\frac{\omega}{n\sigma V_0}\right)^2 + a_2\left(\frac{\omega}{n\sigma V_0}\right)^4 + \cdots\right],$$

$$\alpha = \frac{b_0}{n\sigma}\frac{\omega^2}{V_0^2}\left[1 + b_1\left(\frac{\omega}{n\sigma V_0}\right)^2 + \cdots\right]$$

where the numerical coefficients a_i and b_i depend successively on the eigenvalues λ_i ordered according to their absolute magnitude.

Unfortunately we could not discuss the convergence of this procedure and so one can *not* get an answer to the question what happens at high frequencies for which $\omega/n\sigma V_0$ is of order one. In fact the coefficients a_i and b_i increase rather rapidly, so that numerically the convergence is bad.[2]

3. The Kac successive approximation idea. What is needed is a more precise discussion of the experimental situation as sketched in the beginning of this chapter, and which should clearly be formulated as a
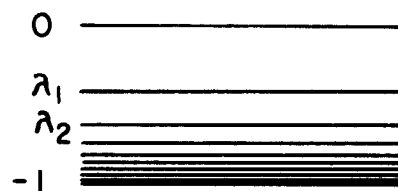

Figure 1

boundary value problem. However, it is simpler to think of the *initial value problem*—given at $t = 0$ the disturbance $h(\mathbf{r}, \mathbf{v}, 0)$, find h at any later time—which also should provide an insight into the behavior of the collective modes of motion of the gas. For the actual equation (3) we have not yet succeeded to find the solution, but it is possible to solve the problem for a simplified version of (3) which is due to Mark Kac.[3]

One can always write (suppressing $\mathbf{r}$ and t):

(9)

$$J(h) = \int d\mathbf{c}_1\, L(\mathbf{c}, \mathbf{c}_1)h(\mathbf{c}_1)$$

$$\text{with:}\quad L(\mathbf{c}, \mathbf{c}_1) = \sum_i \lambda_i \psi_i(\mathbf{c})\psi_i(\mathbf{c}_1)\exp(-c_1^2).$$

Think especially of the quasi-Maxwell model for which the spectrum is shown again in Fig. 1. Put now in (9) as a kind of zeroth

approximation all $\lambda_i = -1$, except the 5 zero eigenvalues. In first approximation one would then keep the first negative eigenvalue λ_1 and collapse all others in -1, and so on. At *every* stage one can solve the initial value problem and one can also discuss in detail all the normal modes, because the linearized Boltzmann equation now becomes an integral equation with a degenerate kernel. In fact using the completeness relation of the ψ_i, one gets in zeroth approximation from (3) and (9):

(10) $\quad \dfrac{\partial h}{\partial \tau} + n\sigma h + \mathbf{c} \cdot \dfrac{\partial h}{\partial \tau}$

$$= \frac{n\sigma}{\pi^{3,2}} \int d\mathbf{c}_1 \exp(-c_1^2)\left[1 + 2\mathbf{c} \cdot \mathbf{c}_1 + \frac{2}{3}\left(c^2 - \frac{3}{2}\right)\left(c_1^2 - \frac{3}{2}\right)\right]h(\mathbf{c}_1)$$

and this should also be the zeroth approximation for *any* molecular model for which the range of the forces is finite.

To simplify the algebra as much as possible I will discuss instead of (10), the equation:

(11) $\quad \dfrac{\partial h}{\partial \tau} + \gamma h + c\dfrac{\partial h}{\partial x} = \dfrac{\gamma}{(2\pi)^{1/2}} \int_{-\infty}^{\infty} dc_1 \exp(-c_1^2/2)(1 + cc_1)h(c_1)$

which is a kind of one-dimensional version of (10). It is related to a one-dimensional Boltzmann-like equation, which was also proposed by M. Kac and it can be obtained by a mutilation of the linearized form of this equation.[4] The mathematics of (10) and (11) are quite similar and also the results are similar, but everything is much simpler for (11).

Since in (11) the coefficients are independent of x, one can always make a Fourier transformation in x. Put:

$$h_k(c, \tau) = \int_{-\infty}^{\infty} dx \, e^{-ikx}h(x, c, \tau);$$

then (11) becomes:

(12) $\quad \dfrac{\partial h_k}{\partial \tau} + (\gamma + ikc)h_k = \dfrac{\gamma}{(2\pi)^{1/2}} \int_{-\infty}^{\infty} dc_1 \exp(-c_1^2/2)(1 + cc_1)h_k(c_1, \tau).$

To solve the initial value problem one can use two methods: (1) the *Laplace transform method* in τ, which brings in immediately the initial value of h_k, or (2) the *method of normal modes*, in which the initial distribution must be developed (provided the normal modes form a complete set) and from which the further temporal development then follows immediately.

Of course, if you do it right the two methods will always give the same answer. I will give some details of *both* methods, mainly because for the quite analogous problem of plasma oscillations there has been some confusion in the literature which only recently has been completely dispelled by K. M. Case (Ann. Phys. 7 (1959) 349). Before embarking on this, note that from (11) still follows by multiplying with $e^{-c^2/2}$ and integrating over c:

$$\frac{\partial \rho}{\partial \tau} + \frac{\partial \phi}{\partial x} = 0 \tag{13}$$

with

$$\rho(x, \tau) = \int_{-\infty}^{+\infty} dc\, e^{-c^2/2} h(x, c, \tau),$$

$$\phi(x, \tau) = \int_{-\infty}^{+\infty} dc\, e^{-c^2/2} c h(x, c, \tau) \tag{14}$$

or after a Fourier transformation in x in obvious notation:

$$\frac{\partial \rho_k(\tau)}{\partial \tau} + ik\phi_k(\tau) = 0. \tag{15}$$

Eq. (13) is a kind of continuity equation or macroscopic equation for this model.

4. The Laplace transform method. Put now:

$$h_{kp}(c) = \int_0^\infty d\tau\, e^{-p\tau} h_k(c, \tau);$$

then one gets from (12):

$$(p + \gamma + ikc)h_{k,p} = h_k(c, 0) + \frac{\gamma}{(2\pi)^{1/2}} (\rho_{kp} + c\phi_{kp}). \tag{16}$$

But from (15) follows:

$$\phi_{kp} = \frac{1}{ik} [\rho_k(0) - p\rho_{kp}].$$

Put this in (16), then:

$$h_{kp} = \frac{h_k(c, 0)}{p + \gamma + ikc} + \frac{\gamma\rho_k(0)}{ik(2\pi)^{1/2}} \frac{c}{p + \gamma + ikc} + \frac{\gamma\rho_{kp}}{(2\pi)^{1/2}} \frac{1 - cp/ik}{p + \gamma + ikc}.$$

Multiply with $\exp(-c^2/2)$ and integrate over c. One then gets a trap for ρ_{kp} and one finds:

$$(18) \qquad \rho_{kp} = \frac{1}{G(p, k)} \int_{-\infty}^{\infty} dc \frac{h_k(c, 0) + \frac{\gamma c}{ik(2\pi)^{1/2}} \rho_k(0)}{p + \gamma + ikc} e^{-c^2/2}$$

with:

$$G(p, k) = 1 - \frac{\gamma}{(2\pi)^{1/2}} \int_{-\infty}^{\infty} dc \frac{1 - cp/ik}{p + \gamma + ikc} e^{-c^2/2}.$$

This put in (17) determines h_{kp} completely in terms of the initial data $h_k(v, 0)$ and $\rho_k(0)$. In fact once $\rho(x, \tau)$ is known by inversion of (18), it is quite easy to invert (16) and one finds:

$$(19) \qquad \begin{aligned} h(x, c, \tau) = e^{-\gamma\tau}h(x - c\tau, v, 0) &+ \frac{\gamma}{(2\pi)^{1/2}} \int_0^\tau d\tau' \, e^{-\gamma\tau'} \\ &\times [\rho(x - c\tau', \tau - \tau') + c\phi(x - c\tau', \tau - \tau')]. \end{aligned}$$

This shows that the influence of the initial distribution damps out in time and that for large τ the distribution function $h(x, c, \tau)$ depends only on the "macroscopic" quantities ρ and ϕ.

5. The normal mode method. This method is perhaps more physical, and anyway it is more familiar. Go back to (12) and seek solutions of the form:

$$h_k(c, \tau) = h_{\omega k}(c) e^{-i\omega\tau}.$$

The function $h_{\omega k}(c)$ is the eigenfunction or normal mode corresponding to the eigenfrequency ω. One gets from (12):

$$(20) \qquad (-i\omega + \gamma + ikc)h_{\omega k} = \frac{\gamma}{(2\pi)^{1/2}} (\rho_{\omega k} + c\phi_{\omega k})$$

and from (15):

$$(21) \qquad \omega\rho_{\omega k} = k\phi_{\omega k}.$$

Because the equation (20) is homogeneous in $h_{\omega k}$, one can always normalize $h_{\omega k}$ so that:

$$(22) \qquad \rho_{\omega k} = \int_{-\infty}^{\infty} dc \, e^{-c^2/2}h_{\omega k}(c) = 1$$

and then from (20) and (21) one gets:

$$(23) \qquad (-i\omega + \gamma + ikc)h_{\omega k} = \frac{\gamma}{(2\pi)^{1/2}} \left(1 + \frac{\omega c}{k}\right).$$

Now one has to watch out!   From (23) one can only conclude:

$$(24) \qquad h_{\omega k}(c) = A\delta\left(c - \frac{\omega + i\gamma}{k}\right) + \frac{\gamma}{(2\pi)^{1/2}} \frac{1 + \omega c/k}{ikc - i\omega + \gamma}$$

where A is arbitrary.   To find the spectrum of eigenfrequencies ω, one has to distinguish two cases:

(a) $\bar{c} = (\omega + i\gamma)/k$ is *real*.   Then from the normalization condition (22) one gets:

$$1 = Ae^{-c^2/2} + \frac{\gamma}{ik(2\pi)^{1/2}} \int_{-\infty}^{\infty} dc \frac{1 + \omega c/k}{c - \bar{c}} e^{-c^2/2}$$

where the principal value of the integral is meant.   This determines A and hence for *fixed real k*, there is a *continuum* of complex eigenfrequencies all with imaginary part equal to $-i\gamma$.   For these modes one can *not* speak of a dispersion law since there is no relation between ω and k.

(b) $\bar{c}$ is *not real*.   Then since c is real, one can omit in (24) the δ-function.   From the normalization condition one then finds:

$$(25) \qquad 1 = \frac{\gamma}{ik(2\pi)^{1/2}} \int_{-\infty}^{\infty} dc \frac{1 + \omega c/k}{c - \bar{c}} e^{-c^2/2}.$$

The right-hand side is an analytic function of ω (always for fixed real k) everywhere, except on the line where the imaginary part of ω is $-i\gamma$. Hence (25) can only be fulfilled for a *discrete* set of values of ω (which may of course be the null set) for each value of k.   For these discrete modes there *is* therefore a dispersion law, and they are the collective modes among which there must be the sound propagation.

The connection between the two methods is clear.   The modes are the poles in the p-plane in the expression (18) for the Fourier-Laplace transform of the density ρ.   Especially Eq. (25) is just the equation $G(-i\omega, k) = 0$.   I will therefore not further elaborate on the derivation of the solution of the initial value problem by means of the normal modes.

Because in this simple case the Eq. (25) for the discrete modes is quite explicit and simple, it is possible to find the discrete modes and to follow them as functions of k.   Put:

$$z = \omega/k, \quad x = \gamma/k, \quad \zeta = z + ix,$$

$$F(\zeta) = \frac{1}{(2\pi)^{1/2}} \int_{-\infty}^{\infty} dc\, e^{-c^2/2} \frac{1}{c - \zeta};$$

then the transcendental equation (25) can be written in the form:

(26) $H(x, \zeta) \equiv x^2\{\zeta F(\zeta) + 1\} + ix\{(\zeta^2 + 1)F(\zeta) + \zeta\} + 1 = 0$

and one can prove (1)

(27) $H^*(x, \zeta) = H(-x, \zeta^*) = H(x, -\zeta^*)$

where the star denotes the complex conjugate.

(2) For $x > 0$ (that is $k > 0$) $H(x, \zeta)$ has no roots in the lower half plane, and zero or two roots (depending on the value of x) in the
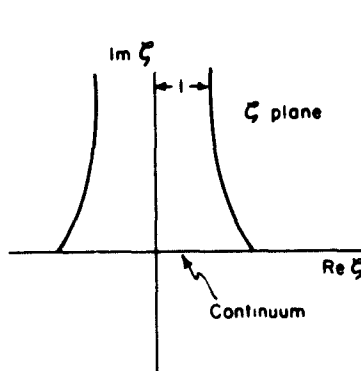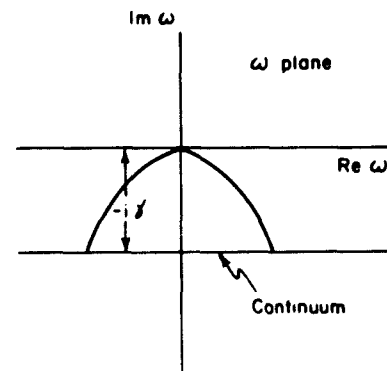

Figure 2   Figure 3

upper half plane.   Because of (27) the two roots (if present) will have the same imaginary part and opposite sign for the real part.   They correspond to a damped sound wave going to the right and to the left. For $x < 0$, that is $k < 0$, one gets because of (27) the complex conjugate solutions.

(3) For x large (or k small, or long wave length) one always has the two roots, and, say, for the one in the first quadrant one gets the *asymptotic* series:

$$z = 1 - \frac{i}{x} + \frac{1}{2x^2} - \frac{6i}{x^3} + \cdots.$$

Putting $\omega = \omega_1 - i\alpha$, this leads to the dispersion law

$$V = \frac{\omega_1}{k} = 1 + \frac{k^2}{2\gamma^2} + \cdots$$

and an absorption coefficient:

$$\alpha = \frac{k^2}{\gamma}\left(1 + \frac{6k^2}{\gamma^2} + \cdots\right)$$

which are similar to the series expansions (8) and which are in fact identical with what one would obtain by applying the Wang-Chang method to Eq. (11).

(4) For decreasing x (or decreasing wave length) V and α increase monotonically till $x = x_{crit} = 0.724 \cdots$. For $x < x_{crit}$ there are no more discrete modes. The paths of the two roots are shown in Fig. 2 in the ζ-plane and in Fig. 3 in the ω-plane. The velocity increases about 10% and the damping increases until it has become as large as for the continuum modes. A similar discussion can be carried out for the more realistic three-dimensional equation (10). The normal mode spectrum consists of a continuum for which the imaginary part of ω_0 is equal to $-n\sigma$, and three discrete modes if $x = n\sigma/k$ is sufficiently large. For $x \to \infty$, these modes correspond to $z = \omega_0$, $k = 0$, $\pm(5/6)^{1/2}$, which are the same as found by the zero approximation of the Wang-Chang determinant (7). For smaller x or shorter wave length one obtains series expansions like (8) for the propagating mode but now one can prove that these series are asymptotic. The third mode, that is the one for which z becomes zero for $x \to \infty$, always is purely imaginary and is not a propagating mode. It can perhaps be called a diffusion mode. There is again a critical value of x for which the damping of the propagating modes has become $n\sigma$ so that they then merge with the continuum. The paths of the discrete zero's seem more complex and need further investigation. It may be that V as function of k will go through a maximum before the critical value of k is reached.

From the physical point of view, it seems to me that the qualitative features of the results, namely: the existence of the continuum (or of single particle modes), sound as one of the discrete modes, the existence of a critical frequency for the sound modes are probably general and are physically reasonable consequences of the existence of a total cross-section; that is, of a lower bound of the spectrum of relaxation times. I am very hopeful that it will lead to a real explanation of what sound *is* at very high frequencies and will help to explain the Greenspan experiments and perhaps will suggest other experiments.

NOTES ON CHAPTER V

1. M. Greenspan, J. Acoust. Soc. Am. **22** (1950) 568. In the actual experiments the frequency of the sound was kept fixed and the mean free path λ was varied by changing the pressure of the Helium gas. Since the relevant parameter is λ/Λ this is equivalent to changing the frequency while keeping the pressure of the gas constant. The restriction to *mono-atomic* gases should be emphasized. For poly-atomic gases there is an additional cause for the dispersion and absorption of sound, which is due to the lag in the transfer of the translational energy into internal energy, and which usually completely masks the dispersion of sound with which we are concerned here.

2. For the detailed discussion we refer to the report cited in Note 7, Chapter IV. The calculations were done for the real Maxwell model. Since in this case there is no total cross-section σ, another form for the dimensionless parameter of order λ/Λ in the development is needed. We chose $\mu\omega/\rho V_0^2$, where μ is again the viscosity coefficient. The results were:

$$\frac{1}{V} = \frac{1}{V_0}\left\{1 - \frac{215}{72}\left(\frac{\mu\omega}{\rho V_0^2}\right)^2 + \frac{4,115,101}{2^7 \cdot 3^4 \cdot 7}\left(\frac{\mu\omega}{\rho V_0^2}\right)^4 - \cdots\right\}$$

$$= \frac{1}{V_0}\left\{1 - 2.99\left(\frac{\mu\omega}{\rho V_0^2}\right)^2 + 56.7\left(\frac{\mu\omega}{\rho V_0^2}\right)^4 - \cdots\right\},$$

$$\alpha = \frac{\mu\omega^2}{\rho V_0^3}\left\{\frac{7}{6} - \frac{5155}{432}\left(\frac{\mu\omega}{\rho V_0^2}\right)^2 + \cdots\right\}$$

$$= \frac{\mu\omega^2}{\rho V_0^3}\left\{1.17 - 11.9\left(\frac{\mu\omega}{\rho V_0^2}\right)^2 + \cdots\right\}$$

which shows how fast the coefficients increase.

3. None of this work has as yet been published. A joint publication is in preparation.

4. The one-dimensional Boltzmann-like equation proposed by M. Kac (Proceedings of the Third Berkeley Symposium on Mathematics, Statistics and Probability, Vol. 3, pp. 171–193) has the form:

$$\text{(a)} \quad \frac{\partial f}{\partial t} + v\frac{\partial f}{\partial x} = \nu\int_{-\infty}^{+\infty} dv_1 \int_{-\pi}^{+\pi} d\theta\, F(\theta)\{f(x, v', t)f(x, v_1', t)$$

$$- f(x, v, t)f(x, v_1, t)\}$$

99

where $v' = v \cos \theta + v_1 \sin \theta$, $v'_1 = -v \sin \theta + v_1 \cos \theta$ and where $F(\theta) = F(-\theta)$ is a dimensionless "collision" probability. Just as the real Boltzmann equation it leads to an equilibrium distribution:

$$f_0 = A \, e^{-\beta v^2}$$

and by linearizing, putting $f = f_0(1 + h(x, v, t))$, one obtains:

(b)

$$\frac{\partial h}{\partial \tau} + c \frac{\partial h}{\partial x} = \nu A J(h),$$

$$J(h) = \int_{-\infty}^{+\infty} dc_1 \exp(-c_1^2/2) \int_{-\pi}^{+\pi} d\theta \, F(\theta)(h' + h'_1 - h - h_1)$$

with $c = v(2\beta)^{1/2}$ and $\tau = t(2\beta)^{1/2}$. It is easy to show that the eigenfunctions of the dimensionless linear operator $J(h)$ are the Hermite polynomials $H_n(c)$ (also sometimes written $He_n(c)$, since the weight function is $\exp(-c^2/2)$) and that the corresponding eigenvalues are:

(c) $$\lambda_n = (2\pi)^{1/2} \int_{-\pi}^{+\pi} d\theta \, F(\theta)\{(\cos \theta)^n + (-1)^n(\sin \theta)^n - 1 - \delta_{n0}\}.$$

In terms of the eigenfunctions one can write $J(h)$ in the form:

(d) $$J(h) = \int_{-\infty}^{+\infty} dc_1 \, L(c, c_1)h(c_1)$$

with:

$$L(c, c_1) = \sum_{n=0}^{\infty} \frac{\lambda_n}{n!(2\pi)^{1/2}} H_n(c)H_n(c_1) \exp(-c_1^2/2)$$

which is similar to Eq. (9) of the text.

The mutilation of the linearized equation starts from the form (d) of $J(h)$. Putting $\lambda_0 = \lambda_1 = 0$ and all other eigenvalues equal to $-\gamma/\nu A$ leads to Eq. (11) of the text. It should be pointed out that this mutilation is *not* analogous to what was done in the three-dimensional case, because from (c) follows that $\lambda_0 = \lambda_2 = 0$, while all other eigenvalues are negative and converging to:

$$-(2\pi)^{1/2} \int_{-\pi}^{+\pi} d\theta \, F(\theta).$$

In the Kac successive approximation method applied to (d) one would

put therefore in zeroth approximation $\lambda_0 = \lambda_2 = 0$ and all other eigenvalues equal to $-\gamma/\nu A$. This leads to the equation:

$$\frac{\partial h}{\partial t} + \gamma h + c \frac{\partial h}{\partial x} = \frac{\gamma}{(2\pi)^{1/2}} \int_{-\infty}^{+\infty} dc_1 \exp(-c_1^2/2)$$
$$\times \left\{ 1 + \frac{1}{2}(c^2 - 1)(c_1^2 - 1) \right\} h(c_1).$$

However it can be shown that this equation does *not* lead to collective modes which are similar to sound.

The Chapman-Enskog Development

1. Introduction. We now return to the general non-linear Boltzmann equation:

$$(1) \qquad \frac{\partial f}{\partial t} + \mathbf{v} \cdot \frac{\partial f}{\partial \mathbf{r}} + \mathbf{a} \cdot \frac{\partial f}{\partial \mathbf{v}} = \int d\mathbf{v}_1 \int d\Omega \, g I(g, \theta)[f' f_1' - f f_1]$$

discussed in Chapter IV, and we will consider the general problem of how the usual macroscopic description of the gas in terms of the hydrodynamical equations is contained in the Boltzmann equation (1). This problem has a long history and both Maxwell and Boltzmann have given it a great deal of attention. The first completely satisfactory solution was given in the dissertation of Enskog in 1917, which was inspired by Hilbert, and independently by Chapman, who used another method which goes back to Maxwell but which led to the same conclusions.[1] I will only try to sketch this theory, and I want to emphasize the mathematical features, which I think are quite curious and fundamental. From the physical point of view, this theory constitutes one of the few successful descriptions of a class of non-equilibrium phenomena in terms of the intermolecular forces.

2. The general conservation laws. The first step is to derive from (1) the so-called transport equation for a quantity $\psi(\mathbf{v})$ which a molecule can carry "on its back". Defining:

$$(2) \qquad \bar{\psi}(\mathbf{r}, t) \equiv \frac{\int d\mathbf{v} \, \psi f}{\int d\mathbf{v} f} = \frac{1}{n} \int d\mathbf{v} \, \psi f$$

where $n(\mathbf{r}, t)$ is the number density, one gets from (1) by multiplying with ψ and integrating:

$$
\begin{aligned}
(3) \quad & \frac{\partial}{\partial t}(n\bar{\psi}) + \frac{\partial}{\partial x_\alpha}(n\overline{v_\alpha \psi}) - n a_\alpha \overline{\frac{\partial \psi}{\partial v_\alpha}} \\
& \qquad = \frac{1}{4} \int d\mathbf{v} \int d\mathbf{v}_1 \int d\Omega \, g I(g, \theta)(\psi + \psi_1 - \psi' - \psi_1')[f' f_1' - f f_1]
\end{aligned}
$$

where in the collision term the same transformations, used in the proof of Boltzmann's *H*-theorem (see Chapter IV, Note 2) are used again. Take now for $\psi(\mathbf{v})$ successively the five quantities 1, $\mathbf{v}$, v^2 which are conserved in a collision.   For these the right-hand side of (3) vanishes and after a few simple transformations one can write the resulting five equations in the form:

$$(4) \begin{cases} \text{(a)} & \dfrac{\partial \rho}{\partial t} + \dfrac{\partial}{\partial x_\alpha}(\rho u_\alpha) = 0, \\[3mm] \text{(b)} & \rho \dfrac{Du_i}{Dt} \equiv \rho\left(\dfrac{\partial u_i}{\partial t} + u_\alpha \dfrac{\partial u_i}{\partial x_\alpha}\right) = \rho a_i - \dfrac{\partial P_{i\alpha}}{\partial x_\alpha}, \\[3mm] \text{(c)} & \rho \dfrac{D}{Dt}\left(\dfrac{Q}{\rho}\right) + \dfrac{\partial q_\alpha}{\partial x_\alpha} = -P_{\alpha\beta}D_{\alpha\beta} \end{cases}$$

where we have used the index notation with the usual summation convention, and where:

$$\rho(\mathbf{r}, t) = mn \qquad = \text{the mass density};$$

$$u_i(\mathbf{r}, t) = \bar{v}_i \qquad = \text{the average velocity};$$

$$U_i = v_i - u_i \qquad = \text{the thermal velocity};$$

$$Q(\mathbf{r}, t) = \frac{1}{2}\rho\overline{U^2} \qquad = \text{the thermal energy density};$$

$$P_{ij}(\mathbf{r}, t) = \rho\overline{U_i U_j} \qquad = \text{the pressure tensor (obviously symmetric)};$$

$$q_i(\mathbf{r}, t) = \frac{1}{2}\rho\overline{U_i U^2} \qquad = \text{the heat current density};$$

$$D_{ij} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right) = \text{the rate of strain tensor}.$$

The equations (4) express the conservation laws of mass, momentum and energy.[2]   They are a rigorous consequence of the Boltzmann equation, but of course they are still an empty frame, since we do not know how to express the P_{ij} and the q_i in terms of the average flow velocity, the density and the temperature.   Or, in other words, one still has to derive the Newton and Fourier phenomenological laws for the friction and the heat conduction.

3. **The Chapman-Enskog development.**   To do this one has somehow to solve the initial value problem for the Boltzmann equation, since to find the average values P_{ij} and q_i one must know the distribution

function f.   Now we discussed already in Chapter IV that the approach to equilibrium proceeds so to say in *two* stages. Because of the collisions any initial distribution will reach very quickly (in a time of the order of the *mean free time* $t_0 \sim \lambda/(kT/m)^{1/2}$) a *local* Maxwell distribution:

$$(5) \qquad f^{(0)} = n\left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left[-\frac{m}{2kT}(v - u)^2\right]$$

where *the macroscopic variables* n, u and T are still functions of r and t.   In the second stage the slow relaxation of the macroscopic variables to their equilibrium values takes place, and it is this stage which we want to follow in more detail.   Now the argument goes as follows:

1. First note that if one uses (5) to calculate P_{ij} and q_i one gets:

$$q_i = 0, \qquad Q = \frac{3}{2}p,$$

(6)

$$P_{ij} = p\delta_{ij} \quad \text{with} \quad p = nkT$$

so that (4) becomes:

$$(7) \begin{cases} \text{(a)} & \frac{\partial\rho}{\partial t} + \text{div}(\rho u) = 0, \\[2mm] \text{(b)} & \rho\frac{Du}{Dt} = \rho a - \text{grad}\, p, \\[2mm] \text{(c)} & \frac{D}{Dt}(\rho T^{-3/2}) = 0 \end{cases}$$

which are the ideal, or Euler hydrodynamical equations with adiabatic temperature changes and with an equation of state which is still the ideal gas law.

2. Of course the two stages of the relaxation to equilibrium are *not* sharply separated, so that one must *not* expect that after a time of order t_0 the distribution function is precisely of the form (5).   Instead it seems more reasonable to put in Eq. (1):

$$(8) \qquad f = f^{(0)}[1 + \phi(r, v, t)]$$

and to keep in the collision term only terms linear in ϕ. Finally, since it is the streaming term in (1) acting on n, u and T which causes the deviation ϕ from the local Maxwell distribution (5), it is sufficient to put only $f^{(0)}$ in these streaming terms.   Thus one is led to:

$$(9) \qquad \left(\frac{\partial}{\partial t} + v_\alpha\frac{\partial}{\partial x_\alpha} + a_\alpha\frac{\partial}{\partial v_\alpha}\right) f^{(0)} = f^{(0)}C(\phi)$$

where:

$$C(\phi) = \int d\mathbf{v}_1 \, f_1^{(0)} \int d\Omega \, g I(g, \theta)[\phi' + \phi_1' - \phi - \phi_1]$$

is the same linearized collision operator introduced in Chapter IV. Note however the *different* way in which one now has linearized the Boltzmann equation. The resulting equation (9) is an *inhomogeneous* linear integral equation, in contrast to the homogeneous equation discussed in the previous chapter.

3. One now runs into the following trouble. The homogeneous equation $C(\phi) = 0$ has the five solutions 1, $\mathbf{v}$, and v^2 (which I will call ψ_i), and therefore (9) has in general no solution. The solubility conditions are that the left-hand side of (9) must be orthogonal to the ψ_i and these five conditions turn out to be the Euler equations (7) for n, $\mathbf{u}$ and T with $p = nkT$.[3] These equations allow us to express the *time* derivatives of the macroscopic variables in terms of their *spatial* derivatives and doing this one then finds:[4]

$$(10) \quad \left(\frac{\partial}{\partial t} + v_\alpha \frac{\partial}{\partial x_\alpha} + a_\alpha \frac{\partial}{\partial v_\alpha}\right) f^{(0)} = f^{(0)}\left[\frac{1}{T}\frac{\partial T}{\partial x_\alpha} U_\alpha\left(\frac{m}{2kT} U^2 - \frac{5}{2}\right) \right.$$
$$\left. + \frac{m}{kT} D_{\alpha\beta}\left(U_\alpha U_\beta - \frac{1}{3}\delta_{\alpha\beta}U^2\right)\right]$$

where $U_i = v_i - u_i$ is again the thermal velocity. With (10) for the left-hand side of (9), this equation *has* a solution of course, which is also unique if we require that:

$$(11) \qquad \int d\mathbf{v} \, \psi_i f^{(0)}\phi = 0$$

which means physically that the macroscopic variables must always be determined from $f^{(0)}$ alone.

4. With the solution for ϕ one then can calculate the pressure tensor P_{ij} and the heat flux q_i for which one finds the well-known Newton and Fourier laws:

$$(12) \qquad P_{ij} = p\delta_{ij} - 2\mu\left(D_{ij} - \frac{1}{3} D_{\alpha\alpha}\delta_{ij}\right),$$
$$q_i = \kappa \frac{\partial T}{\partial x_i}$$

but with *known* values for the viscosity and heat conduction coefficients μ and κ. Putting (12) into the general conservation laws (4) then leads to the Navier-Stokes equations of hydrodynamics.

4. Solution of the integral equation (9). To find the solution for ϕ is the hardest part of the theory. To give you some idea how it goes let me consider again the quasi-Maxwell model. Since the right-hand side of (10) and also $f^{(0)}$ depend only on the thermal velocity U_i, ϕ will also depend only on U_i. Using dimensionless velocity variables:

$$\mathbf{c} = \left(\frac{m}{2kT}\right)^{1/2} \mathbf{U}.$$

Eq. (9) becomes:

$$(13) \quad \frac{1}{T}\frac{\partial T}{\partial x_\alpha} c_\alpha\left(c^2 - \frac{5}{2}\right) + 2D_{\alpha\beta}\left(\frac{m}{2kT}\right)^{1/2}\left(c_\alpha c_\beta - \frac{1}{3}\delta_{\alpha\beta}c^2\right) = n\sigma J(\phi)$$

with:

$$J(\phi) = \frac{1}{\pi^{3/2}}\int d\mathbf{c}_1\, e^{-c_1^2} \int d\Omega\, F(\theta)\, [\phi' + \phi_1' - \phi - \phi_1].$$

The conditions (11) are equivalent to:

$$(14) \qquad\qquad \int d\mathbf{c} \begin{Bmatrix} 1 \\ \mathbf{c} \\ c^2 - \dfrac{3}{2} \end{Bmatrix} e^{-c^2}\phi(\mathbf{c}) = 0.$$

Eq. (13) is especially simple for the Maxwell model, since the functions $c_i(5/2 - c^2)$ and $c_i c_j - (1/3)\delta_{ij}c^2$ which occur on the left-hand side of (13) are eigenfunctions of the operator $J(\phi)$. In the notation of Chapter IV they are ψ_{11m} (with $m = 0, \pm 1$) and ψ_{02m} (with $m = 0, \pm 1, \pm 2$). Since furthermore 1, $\mathbf{c}$, $c^2 - 3/2$ are the eigenfunctions ψ_{000}, ψ_{01m} and ψ_{100} a linear combination of the functions ψ_{11m} and ψ_{02m} will also fulfill the condition (14). Hence one easily sees that an *exact* solution of (13) is:

(15)

$$\phi(\mathbf{c}) = \frac{1}{n\sigma\lambda_{11}}\frac{1}{T}\frac{\partial T}{\partial x_\alpha} c_\alpha\left(c^2 - \frac{5}{2}\right) + \frac{2}{n\sigma\lambda_{02}}\left(\frac{m}{2kT}\right)^{1/2} \cdot D_{\alpha\beta}\left(c_\alpha c_\beta - \frac{1}{3}\delta_{\alpha\beta}c^2\right)$$

where the eigenvalues λ_{11} and λ_{02} can be found from the general formula (24) of Chapter IV. This formula gives:

$$(16) \qquad\qquad \lambda_{11} = \frac{2}{3}\lambda_{02} = -\frac{1}{2}\int d\Omega\, \sin^3\theta F(\theta).$$

One then finds:

$$q_i = \frac{1}{2}\rho\overline{U_i U^2} = \frac{nm}{2\pi^{3/2}}\left(\frac{2kT}{m}\right)^{3/2}\int d\mathbf{c}\, e^{-c^2}\phi(\mathbf{c})c_i c^2$$

$$= \frac{5}{4}\frac{mk}{\sigma\lambda_{11}}\left(\frac{2kT}{m}\right)^{1/2}\frac{\partial T}{\partial x_i},$$

$$P_{ij} = \rho\overline{U_i U_j} = p\delta_{ij} + \frac{2nkT}{\pi^{3/2}}\int d\mathbf{c}\, e^{-c^2}\phi(\mathbf{c})c_i c_j$$

$$= p\delta_{ij} + \frac{m}{\sigma\lambda_{02}}\left(\frac{2kT}{m}\right)^{1/2}\left(D_{ij} - \frac{1}{3}D_{\alpha\alpha}\delta_{ij}\right).$$

One gets therefore the Fourier and Newton laws (12), and one obtains for the heat conductivity and the viscosity coefficients the explicit expressions:

$$(17) \qquad \kappa = -\frac{5}{4}\frac{mk}{\sigma\lambda_{11}}\left(\frac{2kT}{m}\right)^{1/2}, \qquad \mu = -\frac{m}{2\sigma\lambda_{02}}\left(\frac{2kT}{m}\right)^{1/2}$$

which are both positive since λ_{11} and λ_{02} are negative. Both are *independent* of the density and, therefore, functions of the temperature alone. The independence of density is one of the classical results of the kinetic theory of gases and is in accord with experiment. The temperature dependence is different for different molecular models. The dependence $\sim T^{1/2}$ which holds according to (17) for the quasi-Maxwell model (if σ is taken independent of T), is also valid for the elastic sphere model.[5] It only agrees qualitatively with experiment.

From (17) one still finds:

$$(18) \qquad\qquad \kappa = \frac{15}{4}k\mu = \frac{5}{2}c_v\mu$$

which is confirmed very well for mono-atomic gases; 5/2 is the so-called Eucken constant.

Also for other molecular models, in fact for *any* differential cross-section $I(g, \theta)$ it is possible to find the solution of the integral equation (9). The best method (first suggested by Burnett) is to develop ϕ always in the eigenfunctions ψ_{rlm} of the Maxwell model. For the coefficients one then gets an infinite set of linear equations, which can be solved successively and at least for repulsive forces inversely proportional to some power of r, the convergence of this procedure has been established.[6]

It should be emphasized that one thus obtains κ and μ expressed *explicitly* in terms of $I(g, \theta)$ and hence in terms of the force law. One

can therefore predict the magnitude and temperature dependence of κ and μ if one knows the intermolecular forces as deduced, say, from the second virial coefficient. Hirschfelder and co-workers have made such calculations and they got quite a good check with experiment. I think there is no doubt that one has found in this way the right explanation of the non-equilibrium macroscopic phenomena of internal friction and heat conduction of a gas.

5. Higher approximations; general form of the development. The Chapman-Enskog development is a successive approximation or perturbation method (with the local Maxwell distribution (5) as the zeroth order) which can be continued in a systematic way. Since the formulas are a bit long, let me only say that in the nth order one gets for the deviation $\phi^{(n)}$ from $f^{(0)}$ an inhomogeneous integral equation of the same form as (9), that is:

$$(19) \qquad f^{(0)}C(\phi^{(n)}) = L_n$$

where L_n depends on the lower order deviations. The solubility conditions are (or better, the method is so arranged *that* they are) the hydrodynamical equations for the macroscopic quantities found in the previous order, just as the solubility conditions for (9), that is for

$$f^{(0)}C(\phi^{(1)}) = L_1$$

are the zero-order or Euler hydrodynamical equations. Together with an expansion of the distribution function of the form:

$$(20) \qquad f = f^{(0)}(1 + \phi^{(1)} + \phi^{(2)} + \cdots)$$

one obtains therefore *successive order hydrodynamical equations*: 0th order Euler, 1st order Navier-Stokes, 2nd order Burnett equations, and so on.

What is the expansion parameter? It turns out that the expansion (20) can be written symbolically as:

$$f = f^{(0)}[1 + a_1(v)(\lambda\nabla) + a_2(v)(\lambda\nabla)^2 + \cdots]$$

where $\lambda \sim (n\sigma)^{-1}$ is the mean free path, and the gradient acts on the macroscopic variables $u(r, t)$ and $T(r, t)$. Compare Eq. (15) for the first approximation. In the second approximation one gets both second derivatives of u and T and squares of the first derivatives. One can therefore say that the expansion parameter is the relative change of the macroscopic variables over a mean free path. I will call it the *uniformity parameter* θ. Only if this parameter is small, that is if the

u and T vary slowly, will the expansion show a semblance of convergence. For sound waves $\theta \sim \lambda/\Lambda$, so that the Chapman-Enskog development can be expected to give expansions of the velocity and absorption coefficient as discussed in Chapter V. In fact if one calculates say with the Maxwell model the dispersion law of sound from the successive order hydrodynamical equations, then one obtains the *same* expansion as found by the Wang-Chang method. Clearly for strong shock waves where $\theta \sim \lambda/d \cong 1$, d = thickness of the shock, the Chapman-Enskog development will *not* give a good approximation.

Finally note that the successive order hydrodynamical equations are *always* of the *first* order in the time derivatives of the macroscopic variables, but are successively of *higher order* in the space derivatives. If one wants to apply these equations to the flow of the gas around solid bodies or between solid walls, the question of the boundary conditions has to be answered. More and more conditions are clearly required and one can expect therefore successive boundary layer phenomena similar to the well-known Prandtl boundary layer theory which is so characteristic for the approximation of the Navier-Stokes equations by the (lower order) Euler equations. However beyond the Navier-Stokes equations this question has not been investigated systematically, which is one of the reasons why the number of applications of the Burnett equations has been very limited. Physically it is reasonable and customary to assume that the molecules which hit the wall are partially specularly reflected and that the remaining ones are re-emitted by the wall with a Maxwell distribution with a temperature and average velocity determined by the wall. However, it is not clear how one can express this picture in terms of boundary conditions on the macroscopic variables which at every stage would insure an unique solution of the flow problem.

6. The character of the Chapman-Enskog development. Let me summarize in more general terms what we have found so far. By means of a successive approximation method, we have obtained a solution of the Boltzmann equation of the form:

$$(21) \qquad f = f^{(0)}(\mathbf{r}, \mathbf{v}|n, \mathbf{u}, T) + f^{(1)}(\mathbf{r}, v|n, \mathbf{u}, T) + \cdots$$

where each approximation $f^{(k)}$ is a function of $\mathbf{r}$, $\mathbf{v}$ and of the macroscopic variables n, $\mathbf{u}$, T and their spatial derivatives. The $f^{(k)}$ do *not* depend on the time explicitly; in fact, remember that at any stage we eliminated the time derivatives by means of the corresponding lower order hydrodynamical equations. The time dependence is completely governed by the time dependence of the macroscopic variables and

these are determined by the hydrodynamical equations of successive order which are obtained at the same time as (21), and which are of the form:

$$\frac{\partial n}{\partial t} = - \frac{\partial}{\partial x_\alpha} (nu_\alpha),$$

(22)
$$\frac{\partial u_i}{\partial t} = V_i^{(1)}(\mathbf{r}|n, \mathbf{u}, T) + V_i^{(2)}(\mathbf{r}|n, \mathbf{u}, T) + \cdots,$$

$$\frac{\partial T}{\partial t} = \Theta^{(1)}(\mathbf{r}|n, \mathbf{u}, T) + \Theta^{(2)}(\mathbf{r}|n, \mathbf{u}, T) + \cdots.$$

Here again the successive approximations $V_i^{(k)}$ and $\Theta^{(k)}$ in the equation of motion and in the energy equation depend on n, $\mathbf{u}$, T and their spatial derivatives but they do *not* depend on the time explicitly. Both in (21) and (22) the successive orders may be considered to correspond to successive powers of the *uniformity parameter* θ, which is of the order:

(23)
$$\theta \simeq \lambda/L \simeq t_0/T_0$$

where λ = mean free path; $t_0 \simeq \lambda/(kT/m)^{1/2}$ = mean free time or average time between collisions; $L \simeq \psi/\text{grad } \psi$ with ψ any macroscopic quantity; $T_0 \simeq L/V_0$ = macroscopic relaxation time with V_0 = sound velocity.

The curious mathematical feature of the solution (21) of the Boltzmann equation is that apparently the *whole* temporal development of f is determined by giving the initial values of n, $\mathbf{u}$ and T (which according to (22) determine all later values), while from the Boltzmann equation itself follows that one needs the *whole* initial distribution $f(\mathbf{r}, \mathbf{v}, 0)$, which is of course much more information than just the first five moments in velocity, $n(\mathbf{r}, 0)$, $u(\mathbf{r}, 0)$ and $T(\mathbf{r}, 0)$. Since Hilbert pointed out this feature of the solution (21), I usually call it the Hilbert paradox.[7]

Physically one must expect that an initial distribution $f(\mathbf{r}, \mathbf{v}, 0)$ in a time of order t_0 relaxes to a solution of the form (21), *whatever* the initial distribution is. Or one can say that after a time of order t_0 (initial chaotization period) a *contraction* of the description of the state of the gas is possible, in which the temporal development will be determined by much fewer variables. And the reason that these variables are the macroscopic variables n, $\mathbf{u}$ and T, is clearly because they correspond to the five quantities 1, $\mathbf{v}$ and v^2 which are conserved in a collision. Therefore the collisions can not affect the n, $\mathbf{u}$ and T

directly. They will stay constant in a time of order t_0 and in this sense one can say that they are constants of the motion. They will change with time only "secularly" through the change of the distribution function and after a while they therefore completely govern the temporal development of the state of the gas.

In my opinion, the idea of the contraction of the description of the temporal development of the system, is a very fundamental insight. It reminds one of the description through the "macroscopic" variables $y_1, y_2, \cdots$ in the Boltzmann-Gibbs picture of the approach to equilibrium, which we discussed in Chapter I. However now the variables are not determined more or less arbitrarily by a macroscopic observer, but are determined by the system itself, and it is shown that they form a closed deterministic system for themselves, that is to say that their initial values determine their later values.

Of course this contraction of the description, although very plausible, has not really been proved! One would like to know in which precise sense the solution of the initial value problem of the Boltzmann equation is approximated by the Chapman-Enskog expansion (1), and what the nature of the expansion is. I think it is very likely that the expansion is not convergent but asymptotic (as suggested by the application to the dispersion of sound), and that the approach of the $f(\mathbf{r}, \mathbf{v}, t)$ to a solution of type (1) is exponential or in other words that the difference goes to zero as $\exp(-t/t_0)$. The latter is indicated by the work of Grad (Comm. Pure Appl. Math. 2 (1949) 331). Instead of the Chapman-Enskog expansion, Grad has proposed an approximation procedure in which the deviation ϕ from the local Maxwell distribution $f^{(0)}$ is developed in the appropriate three dimensional Hermite polynomials in the thermal velocity U. The coefficients (which are successive moments of the distribution f) are functions of $\mathbf{r}$ and t, and the Boltzmann equation then leads to partial differential equations in these coefficients. It is now quite striking, that Grad could show that all moments which do *not* correspond to the macroscopic variables n, $\mathbf{u}$ and T (which are the first five moments) decay like $\exp(-t/t_0)$ to the values which would follow from the Chapman-Enskog development. I think it confirms and substantiates the idea of the contraction of the description.

NOTES ON CHAPTER VI

1. D. Enskog, *Kinetische Theorie der Vorgänge in Mässig Ver-
dünnten Gasen*, Dissertation, Uppsala, 1917.

S. Chapman, Philos. Trans. Roy. Soc. London. Ser. A **216** (1916)
279; **217** (1917) 115.

The monograph of S. Chapman and T. G. Cowling (*The Mathe-
matical Theory of Non-uniform Gases*, Cambridge University Press,
1939; 2nd edition, 1955) follows the method of Enskog. We refer
to this book for further details. Compare also the treatment of the
theory by L. Waldmann in the Handbuch der Physik, Vol. XII,
Section E, p. 384 and in the book of J. O. Hirschfelder, C. F. Curtiss
and R. B. Bird (*Molecular Theory of Gases and Liquids*, John Wiley
and Sons, New York, 1954, Chapters 7 and 8).

2. The form of the last equation in (4) is perhaps not quite familiar.
Phenomenologically it can be derived as follows. Consider a certain
portion of the gas of volume Ω, then the work done per second by the
surrounding gas and by the outside forces on the gas inside Ω is:

$$
\text{(a)} \qquad -\iint_{\Sigma} d\sigma_\alpha \, P_{\alpha\beta} u_\beta \,+\, \iiint_{\Omega} d\tau \, \rho a_\alpha u_\alpha
$$

where Σ is the surface of Ω and $d\sigma_i$ is a surface element with the
normal outwards. Using Gauss' theorem, the equation of motion
(Eq. (4b)) and the symmetry of the pressure tensor P_{ij}, one can trans-
form (a) into:

$$
\text{(b)} \qquad \iiint_{\Omega} d\tau \left[-P_{\alpha\beta} D_{\alpha\beta} \,+\, \rho u_\alpha \frac{Du_\alpha}{Dt} \right].
$$

This must be equal to the increase per second of the kinetic and
thermal energy of the gas inside Ω plus the kinetic and thermal energy
which flows out of Ω per second. Let $\varepsilon = (1/2)u^2 + (Q/\rho)$ be the
total energy per gram and let $s = \rho\varepsilon u + q$ be the total energy flux
density. Then one has therefore:

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$$\iiint_\Omega d\tau \left[-P_{\alpha\beta} D_{\alpha\beta} + \rho u_\alpha \frac{Du_\alpha}{Dt} \right] = \iiint_\Omega d\tau \frac{\partial}{\partial t}(\rho\varepsilon) + \iint_\Sigma d\sigma_\alpha s_\alpha$$

$$= \iiint_\Omega d\tau \left[\frac{\partial}{\partial t}(\rho\varepsilon) + \frac{\partial}{\partial x_\alpha}(\rho\varepsilon u_\alpha) + \frac{\partial q_\alpha}{\partial x_\alpha} \right]$$

$$= \iiint_\Omega d\tau \left[\rho \frac{\partial\varepsilon}{\partial t} + \rho u_\alpha \frac{\partial\varepsilon}{\partial x_\alpha} + \frac{\partial q_\alpha}{\partial x_\alpha} \right]$$

$$= \iiint_\Omega d\tau \left(\rho \frac{D\varepsilon}{Dt} + \frac{\partial q_\alpha}{\partial x_\alpha} \right)$$

using the continuity equation.   Since:

$$\rho \frac{D\varepsilon}{Dt} = \rho u_\alpha \frac{Du_\alpha}{Dt} + \frac{D}{Dt}\left(\frac{Q}{\rho} \right)$$

this gives the integral form of Eq. (4c).

3. Although this is almost self-evident from the way the Euler equations (7) follow through (4) from the general transport equation (3), one might as well verify it directly.   The orthogonality of the left side of (9) to $\psi_1 = 1$, leads to:

$$\frac{\partial}{\partial t} \int d\mathbf{v}\, f^{(0)} + \frac{\partial}{\partial x_\alpha} \int d\mathbf{v}\, v_\alpha f^{(0)} + a_\alpha \int d\mathbf{v}\, \frac{\partial f^{(0)}}{\partial v_\alpha} = 0.$$

The last integral is zero and the first two terms clearly give the continuity equation:

(c) $$\frac{\partial n}{\partial t} + \frac{\partial}{\partial x_\alpha}(nu_\alpha) = 0.$$

The orthogonality condition for v_i leads to:

$$\frac{\partial}{\partial t} \int d\mathbf{v}\, v_i f^{(0)} + \frac{\partial}{\partial x_\alpha} \int d\mathbf{v}\, v_i v_\alpha f^{(0)} + a_\alpha \int d\mathbf{v}\, v_i \frac{\partial f^{(0)}}{\partial v_\alpha} = 0.$$

Carrying out the integrals, one obtains:

(d) $$\frac{\partial}{\partial t}(nu_i) + \frac{\partial}{\partial x_\alpha}(nu_i u_\alpha) + \frac{\partial}{\partial x_i}\left(\frac{nkT}{m} \right) - na_i = 0$$

and this becomes the equation of motion (7b) by using (c) and by

putting $p = nkT$.   We leave it to the reader to show that the ortho-gonality condition for $\psi_5 = v^2$ leads to (7c).

4. By differentiating logarithmically one. gets:

$$\frac{1}{f^{(0)}}\left(\frac{\partial}{\partial t} + v_\alpha\frac{\partial}{\partial x_\alpha} + a_\alpha\frac{\partial}{\partial v_\alpha}\right)f^{(0)}$$

(e)
$$= \frac{1}{nT^{-3/2}}\left(\frac{\partial}{\partial t} + v_\alpha\frac{\partial}{\partial x_\alpha}\right)(nT^{-3/2}) + \frac{m}{2kT^2}U^2\left(\frac{\partial T}{\partial t} + v_\alpha\frac{\partial T}{\partial x_\alpha}\right)$$
$$+ \frac{m}{kT}(v_\alpha - u_\alpha)\left(\frac{\partial u_\alpha}{\partial t} + v_\beta\frac{\partial u_\alpha}{\partial x_\beta}\right) - \frac{m}{kT}a_\alpha(v_\alpha - u_\alpha).$$

Now from (7):

$$\frac{\partial}{\partial t}(nT^{-3/2}) = -u_\alpha\frac{\partial}{\partial x_\alpha}(nT^{-3/2}),$$

$$\frac{\partial T}{\partial t} = -u_\alpha\frac{\partial T}{\partial x_\alpha} - \frac{2}{3}T\frac{\partial u_\alpha}{\partial x_\alpha},$$

$$\frac{\partial u_i}{\partial t} = -u_\beta\frac{\partial u_i}{\partial x_\beta} + a_i - \frac{1}{\rho}\frac{\partial p}{\partial x_i}.$$

Substituting these expressions for the time derivatives in (e), and using:

$$\frac{\partial p}{\partial x_i} = kT\frac{\partial n}{\partial x_i} + kn\frac{\partial T}{\partial x_i},$$

$$\frac{\partial}{\partial x_i}(nT^{-3/2}) = T^{-3/2}\frac{\partial n}{\partial x_i} - \frac{3}{2}nT^{-5/2}\frac{\partial T}{\partial x_i}$$

one obtains Eq. (10) of the text, and it is easy to verify that the right-hand side of (10) is orthogonal to 1, U_i and U^2 and therefore to the ψ_i.

5. See Chapman and Cowling, l.c. Chapter 10, where one finds the explicit expressions of μ and κ for various molecular models. For the real Maxwell model μ and κ are proportional to the first power of the temperature. That we found for the quasi Maxwell model a dependence $\sim T^{1/2}$ is clearly due to the artificial assumption that the dimensionless function $F(\theta)$ is independent of the temperature.

6. See again Chapman and Cowling, l.c. Chapters 7, 9 and 10, and for the Lennard-Jones (6-12) potential, Hirschfelder, Curtiss and Bird, l.c. Chapter 8, §4.   The papers of D. Burnett are in the Proc. London Math. Soc. 39 (1935) 385 and 40 (1935) 382.

In first approximation for any differential cross-section $I(g, \theta)$ one

puts ϕ equal to a linear combination of the same functions ψ_{11m} and ψ_{02m} occurring in the solution for the Maxwell model.   Using ordinary units this means that one makes the Ansatz:

(f) $\qquad \phi = \frac{1}{T}\frac{\partial T}{\partial x_\mu} U_\mu\left(\alpha U^2 - \frac{5}{2}\right)\chi_1 + 2\alpha D_{\mu\nu}\left(U_\mu U_\nu - \frac{1}{3}\delta_{\mu\nu}U^2\right)\chi_2$

where $\alpha = m/2kT$, and χ_1, χ_2 are constants.   This leads to the heat flux density:

$$q_i = \frac{m}{2}\int d\mathbf{U}\ U_i U^2 f^{(0)}$$

$$= \frac{m}{2}n\left(\frac{\alpha}{\pi}\right)^{3/2}\frac{1}{T}\frac{\partial T}{\partial x_\mu}\chi_1\int d\mathbf{U}\ U_i U_\mu U^2\left(\alpha U^2 - \frac{5}{2}\right)e^{-\alpha U^2}$$

$$= -\kappa\frac{\partial T}{\partial x_i}$$

with:

(g) $\qquad\qquad\qquad\qquad \kappa = -\frac{5k}{4}\frac{\pi^{3/2}}{\alpha^{5/2}}n\left(\frac{\alpha}{\pi}\right)^{3/2}\chi_1.$

Similarly, the second part of the Ansatz (f) leads to the viscosity coefficient:

(h) $\qquad\qquad\qquad\qquad \mu = -\frac{m\pi^{3/2}}{2\alpha^{5/2}}n\left(\frac{\alpha}{\pi}\right)^{3/2}\chi_2.$

Of course, the Ansatz (f) can now only be an approximate solution of the Enskog integral equation (see Eqs. (9) and (10) of the text):

$$\frac{1}{T}\frac{\partial T}{\partial x_\mu}U_\mu\left(\alpha U^2 - \frac{5}{2}\right) + 2\alpha D_{\mu\nu}\left(U_\mu U_\nu - \frac{1}{3}\delta_{\mu\nu}U^2\right) = C(\phi),$$

$$C(\phi) = n\left(\frac{\alpha}{\pi}\right)^{3/2}\int d\mathbf{U}_1\ e^{-\alpha U_1^2}\int d\Omega\ g I(g,\theta)(\phi' + \phi'_1 - \phi - \phi_1)$$

and in order to determine the Ansatz (f) completely one must still find the quantities χ_1 and χ_2.   To do this we require that they are the first development coefficients in the development in the eigenfunctions ψ_{r1m} $(r = 1, 2\cdots)$ and ψ_{r2m} $(r = 0, 1, 2, \cdots)$ of the Maxwell model. This leads immediately to:

(i) $\qquad \chi_1 = \dfrac{\displaystyle\int d\mathbf{U}\ e^{-\alpha U^2}U_\mu U_\mu\left(\alpha U^2 - \frac{5}{2}\right)^2}{\displaystyle\int d\mathbf{U}\ e^{-\alpha U^2}U_\mu\left(\alpha U^2 - \frac{5}{2}\right)C\left[U_\mu\left(\alpha U^2 - \frac{5}{2}\right)\right]},$

(j) $\qquad \chi_2 = \dfrac{\displaystyle\int d\mathbf{U}\ e^{-\alpha U^2}\left(U_\mu U_\nu - \frac{1}{3}\delta_{\mu\nu}U^2\right)\left(U_\mu U_\nu - \frac{1}{3}\delta_{\mu\nu}U^2\right)}{\displaystyle\int d\mathbf{U}\ e^{-\alpha U^2}\left(U_\mu U_\nu - \frac{1}{3}\delta_{\mu\nu}U^2\right)C\left(U_\mu U_\nu - \frac{1}{3}\delta_{\mu\nu}U^2\right)}.$

The calculation of the integrals is straightforward and we will only indicate some of the details for χ_1. The numerator is:

(k)
$$4\pi \int_0^\infty dU \, U^4 \left(\alpha U^2 - \frac{5}{2}\right)^2 e^{-\alpha U^2} = \frac{15}{4} \frac{\pi^{3/2}}{\alpha^{5/2}}.$$

The denominator by means of the Boltzmann H-theorem transformation can be written as:

(l)
$$-\frac{1}{4} n \left(\frac{\alpha}{\pi}\right)^{3/2} \int\int dU \, dU_1 \, e^{-\alpha(U^2 + U_1^2)} \int d\Omega \, g I(g, \theta)$$

$$\cdot \, \Delta\left[U_\mu\left(\alpha U^2 - \frac{5}{2}\right)\right] \Delta\left[U_\mu\left(\alpha U^2 - \frac{5}{2}\right)\right]$$

where the Δ-symbol means

$$\Delta(f(\mathbf{U})) \equiv f(\mathbf{U}') + f(\mathbf{U}_1') - f(\mathbf{U}) - f(\mathbf{U}_1).$$

Clearly the terms with the factor $5/2$ in the Δ-symbols in (l) can be omitted because of momentum conservation. Introduce now the center of mass velocity $\mathbf{U}_c = (1/2)(\mathbf{U} + \mathbf{U}_1) = (1/2)(\mathbf{U}' + \mathbf{U}_1')$, then:

$$\mathbf{U} = \mathbf{U}_c + \frac{1}{2}\,\mathbf{g}, \qquad\qquad \mathbf{U}' = \mathbf{U}_c + \frac{1}{2}\,\mathbf{g}',$$

$$\mathbf{U}_1 = \mathbf{U}_c - \frac{1}{2}\,\mathbf{g}, \qquad\qquad \mathbf{U}_1' = \mathbf{U}_c - \frac{1}{2}\,\mathbf{g}',$$

$$U^2 + U_1^2 = 2U_c^2 + \frac{1}{2}\,g^2, \qquad d\mathbf{U}\,d\mathbf{U}_1 = d\mathbf{U}_c\,d\mathbf{g},$$

$$\Delta(U_i U^2) = (\mathbf{U}_c \cdot \mathbf{g}')g_i' - (\mathbf{U}_c \cdot \mathbf{g})g_i.$$

The integral over $\mathbf{U}_c$ can then be carried out and (l) becomes after integrating over the directions of $\mathbf{g}$:

(m)
$$-n \left(\frac{\alpha}{\pi}\right)^{3/2} \frac{\pi^{5/2}}{2^{5/2}\alpha^{1/2}} \int_0^\infty dg \, g^7 \exp\left(-\frac{\alpha}{2}g^2\right) \int d\Omega \, (1 - \cos^2\theta) I(g, \theta).$$

This is as far as one can carry out the integral without making special assumptions about $I(g, \theta)$. Introducing (k) and (m) in (i) and the resulting value for χ_1 in the equation (g) for the heat conductivity coefficient gives the final answer:

$$\kappa = \frac{25}{16} c_v (\pi m k T)^{1/2} \frac{1}{\displaystyle\int_0^\infty dG \, G^7 \, e^{-G^2} Q(g)}$$

where:

$$c_v = \frac{3k}{2m}; \qquad G = g\left(\frac{m}{4kT}\right)^{1/2}$$

and $Q(g)$ is the so-called transport cross-section:

$$Q(g) = 2\pi \int_0^\pi d\theta \sin^3 \theta \, I(g, \theta).$$

The calculation of χ_2 and hence of μ goes along similar lines, and one finds:

$$\mu = \frac{5}{8} (\pi m k T)^{1/2} \frac{1}{\int_0^\infty dG \, G^7 \, e^{-G^2} \, Q(g)}$$

so that the relation (18) of the text remains valid in this approximation.

7. Hilbert in his paper on the kinetic theory of gases (*Grundzüge einer Allgemeinen Theorie der Linearen Integralgleichungen*, Teubner Verlag, Leipzig, 1912; Chapter 22) speaks of the macroscopic causality *theorem* in this context. In our opinion the word theorem is confusing, because macroscopic causality (which means that the state of the gas is determined by giving at time $t = 0$ the density, velocity and temperature distribution) is clearly a *requirement* which one imposes on the solution of the Boltzmann equation. The word theorem suggests also that the macroscopic causality has been proved by the Chapman-Enskog development, which is clearly not the case.

The Kinetic Theory of Dense Gases

1. Introduction; the problem of deriving the Boltzmann equation. The recent development of the kinetic theory of dense systems has started from the question how to derive the Boltzmann equation from the basic Liouville theorem. Since the subject is still controversial, let me first try to explain why one would *want* to derive the Boltzmann equation.

It is of course true that the way Boltzmann arrived at his equation, which we presented in Chapter IV, was heuristic and that it therefore invites a critical analysis. Historically the criticism of the kinetic method of Boltzmann was mainly directed toward the *H*-theorem and was an expression of the feeling of discomfort that somehow using reversible mechanical models, Boltzmann had succeeded in explaining the typical irreversible approach to equilibrium. It somehow seemed a swindle! I will not discuss the famous classical objections of Loschmidt and Zermelo, since they were answered by the statistical method of Boltzmann and the Boltzmann-Gibbs picture which evolved from it. But it leaves completely open the question of how the kinetic method and especially the Boltzmann equation fits into the general picture of the approach to equilibrium.

Besides the logical gap, there are also practical reasons why one would like to derive the Boltzmann equation. Clearly the applicability of the Boltzmann equation is limited to sufficiently dilute gases, so that *only binary collisions* have to be taken into account. It is the restriction to binary collisions which has as consequence that the transport coefficients κ and μ are independent of the density. Qualitatively this comes about since if only binary collisions are important the mean free path λ is inversely proportional to the number density (i.e. $\lambda \sim 1/n\sigma$), and, hence, in all transport processes one has an exact compensation of the number of transporting particles ($\sim n$) and the amount transported by each of them ($\sim \lambda$, hence $\sim 1/n$) so that the result is independent of n. If triple and higher order collisions must be taken into account, one would expect that:

(1)
$$\lambda \sim \frac{1}{n\sigma(1 + c_1 n + c^2 n^2 + \cdots)}$$

since the number of triple, quadruple $\cdots$ collisions in which a single given particle takes part will clearly be $\sim n^2, n^3, \cdots$. The compensation of the number of particles transporting and the amount transported by each would no longer be exact, and one would expect virial expansions for the transport coefficients of the form:

(2)
$$\mu = \mu_0(T) + \mu_1(T)n + \mu_2(T)n^2 + \cdots,$$

$$\kappa = \kappa_0(T) + \kappa_1(T)n + \kappa_2(T)n^2 + \cdots$$

where μ_0 and κ_0 are the values given by the Chapman-Enskog theory. In addition one would expect that at higher densities *even for monoatomic gases*, the so-called second viscosity coefficient (or bulk viscosity) would appear ($\sim n^2$, I think, since it will depend on the number of quasi binary molecules). There is considerable experimental material about the density dependence of κ and μ and of the bulk viscosity for dense gases, and at present one is still completely unable to correlate the experiments with theory. In this respect the contrast with the equilibrium theory of non-ideal gases is quite striking. Clearly the expected expansions (2) are quite similar to the virial expansion of the equation of state:

(3)
$$\frac{pv}{kT} = 1 + \frac{B(T)}{v} + \frac{C(T)}{v^2} + \frac{D(T)}{v^3} + \cdots.$$

In fact we saw that $B(T)$ and $\mu_0(T)$, $\kappa_0(T)$ are directly related to each other since they have to do with only binary interactions. Similarly one would expect that the third virial coefficient $C(T)$ would be related to $\mu_1(T)$ and $\kappa_1(T)$, and so on. But, while we *know* the explicit expressions for $C(T)$, $D(T)$, $\cdots$ in terms of the intermolecular forces, a similar expression for the transport virial coefficients is *not* known.

To come back to the Boltzmann equation, it is clear that to develop a theory for the virial expansion of the transport coefficients one must generalize the Boltzmann equation so as to take into account the triple and higher collisions. Unfortunately, lacking Boltzmann's intuition, it has (at least till now!) not been evident how one should do this, and hence one has been forced back to see whether one could "derive" the ordinary Boltzmann equation from a more fundamental point of view, with the hope that this would then also indicate the generalization to higher densities.

In this chapter I will present the ideas and the method of Bogoliubov. I should say that although these ideas are in my opinion very plausible

and although the method has at least the virtue that it gives a definite recipe how to generalize the Boltzmann equation, it is *not* so that they have led to definite results, which are physically so ev:dent or which are so completely in agreement with experiment, that there could not be any doubt about their validity. As a result the subject is still controversial. Other methods to derive the Boltzmann equation have been proposed by Kirkwood and co-workers, by M. S. Green, by Prigogine and co-workers, and by a number of other authors.[1] It seems to me that the various methods begin to converge towards each other and perhaps they will justify the ideas of Bogoliubov. But further clarification is certainly needed!

2. The B-B-G-K-Y hierarchy. Since we do not know how to proceed by intuitive methods, we have to go back to the Liouville equation, which is so to say the basic equation of statistical mechanics. Consider again our system of N particles with known interactions in a volume V. The state of the whole gas is described by the probability distribution in Γ-space $D_N(x_1, x_2, \cdots, x_N; t)$, where $x_i \equiv (\mathbf{r}_i, \mathbf{p}_i)$ denotes the coordinates and momenta of the ith particle. We take this distribution to be normalized to unity:

$$(4) \qquad \int \cdots \int dx_1 \cdots dx_N \, D_N(x_1, \cdots, x_N, t) = 1$$

and require, for a gas of identical particles, that D_N be a symmetric function of $x_1, x_2, \cdots, x_N$. The change of D_N with time is governed by the Liouville equation:

$$(5) \qquad \frac{\partial D_N}{\partial t} = \{H_N, D_N\} \equiv \sum_{i=1}^{N} \left(\frac{\partial H_N}{\partial \mathbf{r}_i} \cdot \frac{\partial D_N}{\partial \mathbf{p}_i} - \frac{\partial H_N}{\partial \mathbf{p}_i} \cdot \frac{\partial D_N}{\partial \mathbf{r}_i} \right)$$

with

$$(6) \qquad H_N = \sum_{i=1}^{N} \left[\frac{\mathbf{p}_i^2}{2m} + U(\mathbf{r}_i) \right] + \sum_{i<j} \phi(|\mathbf{r}_i - \mathbf{r}_j|).$$

Here $U(\mathbf{r}_i)$ is the wall potential (no other outside forces will be assumed) and $\phi(|\mathbf{r}_i - \mathbf{r}_j|)$ is the interaction potential which is assumed to be of the usual van der Waals form discussed in Chapter I.

Instead of using Poisson brackets as in (5) it is convenient to introduce a Hamiltonian operator:

$$\mathscr{H}_N(x_1 \cdots x_N) = \sum_{i=1}^{N} \frac{\mathbf{p}_i}{m} \cdot \frac{\partial}{\partial \mathbf{r}_i} - \sum_{i<j} \Theta_{ij},$$

$$(7)$$

$$\Theta_{ij} = \frac{\partial \phi_{ij}}{\partial \mathbf{r}_i} \cdot \frac{\partial}{\partial \mathbf{p}_i} + \frac{\partial \phi_{ij}}{\partial \mathbf{r}_j} \cdot \frac{\partial}{\partial \mathbf{p}_j},$$

then (5) can be written:

(8)
$$\frac{\partial D_N}{\partial t} = -\mathscr{K}_N D_N.$$

Note that we have omitted the wall potential due to the vessel V, so that strictly (8) is only valid if the particles are inside V. We will soon go to the limit $N \to \infty$, $V \to \infty$, $v = V/N$ finite and then the effect of the walls will drop out completely so that (8) can be used. From (5) or (8) follows by integration a hierarchy of equations for the partial distribution functions:

(9)
$$F_s(x_1, \cdots, x_s) = V^s \int \cdots \int D_N \, dx_{s+1} \cdots dx_N$$

which has been derived by many authors and which I call therefore the B(ogoliubov)-B(orn)-G(reen)-K(irkwood)-Y(von) hierarchy.[2] One finds:

(10)
$$\frac{\partial F_s}{\partial t} + \mathscr{K}_s F_s = \frac{1}{v} \int dx_{s+1} \sum_{i=1}^{s} \Theta_{i,s+1} F_{s+1}.$$

PROOF. Integrating (8) over $x_{s+1} \cdots x_N$ and multiplying with V^s, one obtains:

$$\frac{\partial F_s}{\partial t} + \mathscr{K}_s F_s = V^s \int \cdots \int dx_{s+1} \cdots dx_N \Big\{ - \sum_{i=s+1}^{N} \frac{\mathbf{p}_i}{m} \cdot \frac{\partial}{\partial \mathbf{r}_i}$$
$$+ \sum_{1 \leq i: s+1 \leq j \leq N} \Theta_{ij} + \sum_{s+1 \leq k < l} \Theta_{kl} \Big\} D_N(x_1, \cdots, x_N, t).$$

Since D_N must be assumed to vanish for large $\mathbf{p}_i$ and $\mathbf{r}_i$ the first and third terms in the brackets integrate to zero. The second term, because of the symmetry of D_N can be written in the form:

$$V^s(N - s) \sum_{i=1}^{s} \int dx_{s+1} \, \Theta_{i,s+1} \int dx_{s+2} \cdots dx_N \, D_N$$
$$= \frac{N - s}{V} \sum_{i=1}^{s} \int dx_{s+1} \, \Theta_{i,s+1} F_{s+1}(x_1, \cdots, x_{s+1}, t).$$

Hence in the limit $N \to \infty$, $V \to \infty$, $v = V/N$ and s fixed one obtains the right-hand side of (10).

Since we shall be especially interested in the cases $s = 1$ and $s = 2$, let me write out these cases more explicitly.   One gets:

$$(11) \begin{cases} \text{(a)} \qquad \frac{\partial F_1}{\partial t} + \frac{\mathbf{p}_1}{m} \cdot \frac{\partial F_1}{\partial \mathbf{r}_1} = \frac{1}{v} \int dx_2 \, \Theta_{12} F_2(x_1, x_2, t), \\ \\ \text{(b)} \qquad \frac{\partial F_2}{\partial t} + \left(\frac{\mathbf{p}_1}{m} \cdot \frac{\partial}{\partial \mathbf{r}_1} + \frac{\mathbf{p}_2}{m} \cdot \frac{\partial}{\partial \mathbf{r}_2} - \Theta_{12} \right) F_2 \\ \\ \qquad\qquad\qquad = \frac{1}{v} \int dx_3 (\Theta_{13} + \Theta_{23}) F_3(x_1, x_2, x_3, t). \end{cases}$$

Note that (11a) already smells a bit like the Boltzmann equation. But of course the connection is still far from clear.

3. The ideas of Bogoliubov.   The Liouville equation (5) or the hierarchy (10) to which it is equivalent embodies the mechanical assumptions.   Knowing $D_N(0)$ at $t = 0$, (5) will tell us in principle what D_N is at any later time.   But how does one know $D_N(0)$?   The answer is, I think, that one is only interested in those phenomena which are *independent* of $D_N(0)$, or rather depend only on a few average values over $D_N(0)$.   To see how such a description, essentially independent of $D_N(0)$, can come about we have first to look at the basic relaxation times.   They are:

(a) the time *of* a collision $\tau \sim r_0/v_{\text{av}}$, r_0 = range of the forces (which from now on we will assume to be *purely repulsive*) and v_{av} is some average thermal velocity.

(b) the time *between* collisions. $t_0 = \lambda/v_{\text{av}}$; λ = mean free path.

(c) the macroscopic relaxation time. $T_0 = L/V_0$; L is a macroscopic length and V_0 is the sound velocity ($\simeq v_{\text{av}}$).

In the usual situations: slowly varying macroscopic phenomena, not *too* dense gases (therefore not for liquids for which $r_0 \simeq \lambda$), one will have:

$$(12) \qquad\qquad\qquad \tau \ll t_0 \ll T_0.$$

Now Bogoliubov says that one can expect that after an initial chaotization time of order τ, and for *any* $D_N(0)$ a stage is reached—Bogoliubov calls it the *kinetic stage*—in which the further temporal development of the gas is determined *completely* by the temporal change of the first distribution function $F_1(x, t)$ which in turn is governed by an equation of the form:

$$(13) \qquad\qquad\qquad \frac{\partial F_1}{\partial t} = A(x|F_1)$$

where A depends functionally on F_1 but does *not* depend on the time explicitly. *All* the higher distribution functions F_s depend on the time *only* through F_1 and have therefore the form:

$$(14) \qquad F_s = F_s(x_1, \cdots, x_s|F_1) \quad (s \geq 2).$$

To elucidate, note:

(a) Eqs. (13) and (14) represent a *contraction* of the description of the state of the gas, which is quite analogous to the Chapman-Enskog solution of the Boltzmann equation which describes the second or *hydrodynamical stage* of the total relaxation process. Eq. (13) is analogous to the Ansatz for the hydrodynamical equations (Eq. (22), Chapter VI), and Eq. (14) to the Ansatz for the solution of the Boltzmann equation (Eq. (21), Chapter VI) which we discussed in the previous chapter.

(b) Just as in the hydrodynamical stage the contraction is coupled with an expansion in the uniformity parameter $\theta \cong t_0/T_0$, in the kinetic stage the contraction is coupled with an expansion in powers of $1/v$ (virial expansion). Bogoliubov puts:

$$(15) \qquad A(x|F_1) = A^{(0)}(x|F_1) + \frac{1}{v} A^{(1)}(x|F_1) + \frac{1}{v^2} A^{(2)}(x|F_1) + \cdots,$$

and

$$(16) \qquad F_s = F_s^{(0)}(x_1 \cdots x_s|F_1) + \frac{1}{v} F_s^{(1)}(x_1 \cdots x_s|F_1) + \cdots.$$

Note that the dimensionless parameter in (15) and (16) will of course be of order $r_0^3/v = r_0^3 n = r_0/\lambda$ since $\lambda \sim 1/nr_0^2$. Hence just as in the hydrodynamical stage, the development parameter can be looked upon as the ratio τ/t_0 of the two relaxation times in question. However in practice it is easier to use $1/v$.

(c) The reason that in the kinetic stage F_1 is the basic "secular" variable which governs the temporal development, is because of the fact that the intermolecular forces do not affect F_1 directly. Only for $s \geq 2$ does the streaming term $\mathcal{H}_s F_s$ contain the intermolecular force so that F_s ($s \geq 2$) will change quickly in a time of order τ while the F_1 will stay constant. In the *same* sense therefore as in the hydrodynamical stage and in the time scale t_0 the macroscopic quantities ρ, u and T could be considered constants of the motion, so in the kinetic stage and in the time scale τ the F_1 can be considered to be a constant of the motion.

(d) The connection with the general Boltzmann-Gibbs picture of the approach to equilibrium is I think clear. The contraction is

similar to the description through the "macroscopic" variables $y_1, y_2, \cdots$ except that again the choice of F_1 is determined by the system and *not* by a macroscopic observer, and that one obtains at the same time a closed deterministic description through the kinetic equation (13).

Of course, all this is a program. We will now proceed to work it out, and then you will see also some of the difficulties.

4. Determination of the functionals $F_s^{(l)}$. Substituting the virial expansion (16) for $s = 2$ in the first equation of the BBGKY hierarchy (10) one obtains:

$$\frac{\partial F_1}{\partial t} + \frac{\mathbf{p}_1}{m} \cdot \frac{\partial F_1}{\partial \mathbf{r}_1} = \frac{1}{v} \int dx_2\, \Theta_{12} F_2^{(0)}(x_1, x_2 | F_1)$$
$$+ \frac{1}{v^2} \int dx_2\, \Theta_{12} F_2^{(1)}(x_1, x_2 | F_1) + \cdots.$$

Hence comparing with the kinetic equation (13) and using the virial expansion (15) for $A(x|F_1)$, one gets:

(17a) $$A^{(0)}(x_1|F_1) = -\frac{\mathbf{p}_1}{m}\frac{\partial F_1}{\partial \mathbf{r}_1} = -\mathcal{H}_1 F_1,$$

(17b) $$A^{(1)}(x_1|F_1) = \int dx_2\, \Theta_{12} F_2^{(0)}(x_1, x_2|F_1)$$

and in general:

(17c) $$A^{(l)}(x_1|F_1) = \int dx_2\, \Theta_{12} F_2^{(l-1)}(x_1, x_2|F_1).$$

Since for $s \geq 2$, F_s depends on time only through its functional dependence upon F_1, its time derivative can be expressed in terms of F_1 through the kinetic equation (13). Indeed, for any functional $\psi(x_1, x_2 \cdots |F_1)$ which depends on time only through F_1, $\partial\psi/\partial t$ can be expressed as a new functional of F_1 by forming the formal derivative of ψ with respect to t and then replacing $\partial F_1/\partial t$ by $A(x|F_1)$ wherever it occurs in the resulting functional. If in addition we introduce the virial expansion (15) for $A(x|F_1)$, it is clear that one can write:

(18) $$\frac{\partial}{\partial t}\psi(x_1, x_2 \cdots F_1) = D^{(0)}\psi + \frac{1}{v}D^{(1)}\psi + \cdots$$

where the formal operator $D^{(l)}$ consists in forming the derivative of ψ with respect to t and then replacing $\partial F_1/\partial t$ wherever it occurs by $A^{(l)}(x|F_1)$. Of course, the argument x of $A^{(l)}(x|F_1)$ must be taken as

the argument of $\partial F_1/\partial t$ as it occurs in the differentiation process. Hence, substituting the virial expansion (16) for F_s into the hierarchy (10) for $s > 2$ and equating equal powers of $1/v$ one gets:

(19a) $$D^{(0)}F_s^{(0)} + \mathscr{H}_s F_s^{(0)} = 0$$

and for $l \geqq 1$:

(19b) $$D^{(0)}F_s^{(l)} + \mathscr{H}_s F_s^{(l)} = -\sum_{j=1}^{l} D^{(j)}F_s^{(l-j)} + \int dx_{s+1} \sum_{i=1}^{s} \Theta_{i,s+1}F_{s+1}^{(l-1)}.$$

These equations together with (17) are functional equations for $F_s^{(l)}$ assuming that F_1 is a given function, which is in principle arbitrary. Presumably (19a) will determine $F_s^{(0)}$ and therefore especially $F_2^{(0)}$, which then according to (17b) enables one to find $A^{(1)}$. This in turn allows one to find $D^{(1)}F_s^{(0)}$ and then (19b) for $l = 1$ will give $F_s^{(1)}$ which leads to $A^{(2)}$, and so on.

We now have to discuss in which sense the functional equations (19) determine the functionals $F_s^{(l)}$. We will assume therefore that the right-hand sides of the equations (19) are known functionals of F_1 and we will try to find $F_s^{(l)}$.

The trick Bogoliubov uses to solve a functional equation of the form:

(20) $$D^{(0)}F_s^{(l)} + \mathscr{H}_s F_s^{(l)} = \psi_s^{(l)}(x_1 \cdots x_s | F_1)$$

where $\psi_s^{(l)}$ is a known functional of F_1, is the replacement of the formal operator $D^{(0)}$ by an ordinary derivative with respect to an auxiliary time variable τ. To explain this, we introduce the k-particle *streaming operator*:

(21) $$S_k(x_1 \cdots x_k, \tau) = \exp\{\tau \mathscr{H}_k(x_1 \cdots x_k)\}.$$

It is the time displacement operator over the time τ due to the streaming of the k particles in their $6k$-dimensional phase space under the influence of their mutual interactions. If $(\mathbf{r}_i, \mathbf{p}_i)$ is the phase of the ith particle, then in the motion of the k particles the phase of particle i a time τ later is $S_k(\tau)\mathbf{r}_i$, $S_k(\tau)\mathbf{p}_i$, which is a function of the phases $x_1 \cdots x_k$ of *all* k particles, although usually we will not put this in evidence. If $\chi(x_1 \cdots x_k)$ is an arbitrary function of the phases of the k particles then:

(22) $$S_k(\tau)\chi(x_1 \cdots x_k) = \chi(S_k(\tau)x_1, S_k(\tau)x_2 \cdots S_k(\tau)x_k).$$

Clearly the $S_k(\tau)$ form an additive Abelian one parameter group of

operators; $S_k(\tau_1) \cdot S_k(\tau_2) = S_k(\tau_1 + \tau_2)$; $S_k(-\tau)$ is the inverse of $S_k(\tau)$ and $S_k(0) = 1$. Especially:

$$(23) \qquad S_1(\tau)\chi(x, t) = e^{\tau \mathscr{H}_1}\chi(x, t) = \chi\left(\mathbf{r} + \frac{\mathbf{p}}{m}\tau, \mathbf{p}, t\right).$$

To replace the formal operator $D^{(0)}$ by an ordinary derivative we first note that:

$$\frac{\partial}{\partial t} S_1(\tau)F_1(x, t) = \mathscr{H}_1 e^{\tau \mathscr{H}_1} F_1 = \mathscr{H}_1 S_1(\tau)F_1$$

$$(24)$$

$$= -A^{(0)}(x|S_1(\tau)F_1)$$

using the expression (17a) for $A^{(0)}$. Hence from the definition of the operator $D^{(0)}$ it follows that:

$$(25) \qquad D^{(0)}F_s^{(1)}(x_1 \cdots x_s|S_1(\tau)F_1) = -\frac{\partial}{\partial\tau} F_s^{(1)}(x_1 \cdots x_s|S_1(\tau)F_1).$$

Since the function $F_1(x, t)$ in (20) is arbitrary, we can replace it by $S_1(\tau)F_1$ and using (25) it follows that (20) is equivalent to the differential equation:

$$\frac{\partial F_s^{(1)}(x_1 \cdots x_s|S_1(\tau)F_1)}{\partial\tau} - \mathscr{H}_s F_s^{(1)}(x_1 \cdots x_s|S_1(\tau)F_1)$$

$$(26)$$

$$= -\psi_s^{(1)}(x_1 \cdots x_s|S_1(\tau)F_1).$$

So far nothing has been assumed; one has only transformed (20) into (26) because it is simpler to treat ordinary differential equations than functional differential equations. However in the form (26) one sees that more information is needed to find the $F_s^{(1)}$. Clearly some sort of *initial* or *boundary condition* is required. Bogoliubov *assumes* that for any of the functionals F_s for $s \geqq 2$:

$$(27) \quad \lim_{\tau \to \infty} S_s(-\tau)F_s(x_1 \cdots x_s|S_1(\tau)F_1) = \lim_{\tau \to \infty} S_s(-\tau) \prod_{i=1}^{s} S_1(\tau)F_1(x_i, t).$$

The basic nature of this assumption should be emphasized. What it means is most easily seen by considering the spatial uniform case, since then (see Eq. (23)) the $S_1(\tau)$ operator can be omitted and (27) becomes:

$$\lim_{\tau \to \infty} S_s(-\tau)F_s = \lim_{\tau \to \infty} S_s(-\tau) \prod_{i=1}^{s} F_1(\mathbf{p}_i, t).$$

We can say therefore that if one traces the s particles back in the past where they will be far apart from each other because of the repulsive

forces, we *assume* that their momenta are uncorrelated so that the F_s is a product of F_1's. This is *not* obvious! One might for example just as well think that the same type of independence would hold for the future, that is for $\tau \to -\infty$. We shall soon see that this is not acceptable since it would lead to a Boltzmann equation for which the direct and restituting collisions are interchanged so that the H-function would increase instead of decrease. It is the boundary condition (27) which *selects* the appropriate irreversible solutions of the BBGKY hierarchy (10) of the form (13) and (14). The reason why such a condition is necessary while in the corresponding Chapman-Enskog development there was no need for an analogous condition, is, I think, because the Boltzmann equation is already irreversible while for the Liouville equation (and therefore for the hierarchy) one must *choose* the direction of time for which the continuing phase mixing takes place.[3]

Accepting the boundary condition (27), let us see how the functionals $F_s^{(l)}$ can then be determined. First of all from the virial expansion (16) of the F_s it follows that (27) implies:

$$(28) \begin{cases} \text{(a)} & \lim_{t \to \infty} S_s(-\tau)F_s^{(0)}(x_1 \cdots x_s | S_1(\tau)F_1) \\ & \qquad\qquad = \lim_{t \to \infty} S_s(-\tau) \prod_{i=1}^s S_1(\tau)F_1(x_i, t), \\ \text{(b)} & \lim_{t \to \infty} S_s(-\tau)F_s^{(l)}(x_1 \cdots x_s | S_1(\tau)F_1) = 0 \quad (l \neq 0). \end{cases}$$

Start from (26) and take first $l = 0$, in which case the right-hand side $\psi^{(0)} = 0$ (see Eq. (19a)). The "solution" of (26) is then:

$$F_s^{(0)}(x_1 \cdots x_s | S_1(\tau)F_1) = S_s(\tau)F_s^{(0)}(x_1 \cdots x_s | F_1).$$

Or:

$$F_s^{(0)}(x_1 \cdots x_s | F_1) = S_s(-\tau)F_s^{(0)}(x_1 \cdots x_s | S_1(\tau)F_1).$$

The left-hand side is independent of τ, so one can go to the limit $\tau \to \infty$ and from the boundary condition (28a) one then finds:

$$(29) \qquad F_s^{(0)}(x_1 \cdots x_s | F_1) = \lim_{t \to \infty} S_s(-\tau) \prod_{i=1}^s S_1(\tau)F_1(x_i, t).$$

To find $F_s^{(l)}$ for $l > 0$ from Eq. (26) one argues in the same way. From the general formal "solution" of (26) one gets:

$$F_s^{(l)}(x_1 \cdots x_s | F_1) = S_s(-\tau)F_s^{(l)}(x_1 \cdots x_s | S_1(\tau)F_1)$$
$$+ \int_0^t d\tau_1 \, S_s(-\tau_1)\psi_s^{(l)}(x_1 \cdots x_s | S_1(\tau_1)F_1)$$

and by applying the boundary condition (28b) for $\tau \to \infty$ one sees that the first term on the right-hand side is zero, so that:

$$(30) \qquad F_s^{(1)}(x_1 \cdots x_s | F_1) = \int_0^\infty d\tau_1 \, S_s(-\tau_1) \psi_s^{(1)}(x_1 \cdots x_s | S_1(\tau_1) F_1).$$

Using (29) and (30) the functionals $F_s^{(1)}$ can be determined successively from the basic equation (19).

5. The kinetic equation. Let us now write out according to our recipe the first few terms in the kinetic equation. To simplify the formula, let me introduce the abbreviation:

$$(31) \qquad \mathcal{S}_s(x_1 \cdots x_s) = \lim_{\tau \to \infty} S_s(x_1 \cdots x_s, -\tau) \prod_{i=1}^{s} S_1(x_i, \tau)$$

since this combination of streaming operators occurs all the time. From (29) one gets:

$$F_2^{(0)}(x_1 x_2 | F_1) = \mathcal{S}_2(x_1 x_2) F_1(x_1, t) F_1(x_2, t).$$

Hence substituting in (17b), one can write:

$$
(32)
\begin{aligned}
A^{(1)}(x_1 | F_1) &= \int dx_2 \, \Theta_{12} \mathcal{S}_2 F_1(x_1, t) F_1(x_2, t) \\
&= \int\int d\zeta_1 \, d\zeta_2 \, F_1(\zeta_1, t) F_1(\zeta_2, t) \Omega_2(x_1 | \zeta_1, \zeta_2)
\end{aligned}
$$

with

$$(33) \qquad \Omega_2(x_1 | \zeta_1, \zeta_2) = \int dx_2 \, \Theta_{12} \mathcal{S}_2(x_1, x_2) \delta(x_1 - \zeta_1) \delta(x_2 - \zeta_2).$$

Here $\zeta_i \equiv (\xi_i, \eta_i)$ corresponding to $x_i \equiv (r_i, p_i)$. Clearly the two lines in (32) are equivalent with the definition (33) for Ω_2. The reason for writing $A^{(1)}$ in the form (32) is in order to separate the dependence on the distribution F_1 from the mechanics of the binary interaction which is embodied in the function Ω_2.

Turning now to $A^{(2)}(x_1 | F_1)$, we have first to find $F_2^{(1)}$, which means according to (30) that we have to determine $\psi_2^{(1)}$. From (29) and the definition of the operator $D^{(1)}$, one gets, using the first line of (32) for $A^{(1)}$:

$$
\begin{aligned}
D^{(1)} F_2^{(0)}(x_1, x_2 | F_1) &= \mathcal{S}_2 \{ F_1(x_1, t) A^{(1)}(x_2 | F_1) + A^{(1)}(x_1 | F_1) F_1(x_2, t) \} \\
&= \mathcal{S}_2(1, 2) \int dx_3 \, \{ \Theta_{13} \mathcal{S}_2(1, 3) + \Theta_{23} \mathcal{S}_2(2, 3) \} \prod_{i=1}^{3} F_1(x_i, t)
\end{aligned}
$$

where we have omitted the x's in the arguments of the streaming operators and only indicated the particles involved. Next according to (19b) we need $F_3^{(0)}$ which according to (29) is given by:

$$F_3^{(0)}(x_1, x_2, x_3|F_1) = \mathscr{S}_3(1, 2, 3) \prod_{i=1}^{3} F_1(x_i, t).$$

Altogether one gets:

$$
\begin{aligned}
(34) \quad \psi_2^{(1)}(x_1, x_2|F_1) = \int dx_3 \, [(\Theta_{13} + \Theta_{23}).\mathscr{S}_3(1, 2, 3) \\
- \mathscr{S}_2(1, 2)\{\Theta_{13}.\mathscr{S}_2(1, 3) + \Theta_{23}\mathscr{S}_2(2, 3)\}] \prod_{i=1}^{3} F_1(x_i, t).
\end{aligned}
$$

Putting this in (30) (taking $l = 1$, $s = 2$) gives $F_2^{(1)}(x_1, x_2|F_1)$ and from (17) one then finds $A^{(2)}$. Note that $\psi_2^{(1)}$ and therefore also $F_2^{(1)}$ is symmetric in x_1, x_2. Separating as in (32) the distribution functions F_1 from the dynamics of the triple interactions, one can finally write:

$$(35) \qquad A^{(2)}(x_1|F_1) = \iiint d\zeta_1 \, d\zeta_2 \, d\zeta_3 \prod_{i=1}^{3} F_1(\zeta_i, t)\Omega_3(x_1|\zeta_1, \zeta_2, \zeta_3)$$

with:

$$
\begin{aligned}
(36) \quad & \Omega_3(x_1|\zeta_1, \zeta_2, \zeta_3) \\
& = \int dx_2 \, \Theta_{12} \int_0^{\tau} d\tau \, S_2(1, 2, -\tau) \int dx_3 \, [\ ] \cdot \prod_{i=1}^{3} S_1(x_i, \tau)\delta(x_i - \zeta_i).
\end{aligned}
$$

where [ ] stands for the expression in square brackets in Eq. (34).

I think this shows sufficiently how the successive approximation method works, and how one can determine successively the functionals $F_s^{(l)}$ and $A^{(k)}$. Especially one will get for the kinetic equation:

$$
\begin{aligned}
(37) \quad \frac{\partial F_1}{\partial t} + \frac{\mathbf{p}_1}{m} \frac{\partial F_1}{\partial \mathbf{r}_1} &= \frac{1}{v} \iint d\zeta_1 \, d\zeta_2 \, \Omega_2(x_1|\zeta_1, \zeta_2)F_1(\zeta_1, t)F_1(\zeta_2, t) \\
& + \frac{1}{v^2} \iiint d\zeta_1 \, d\zeta_2 \, d\zeta_3 \, \Omega_3(x_1|\zeta_1, \zeta_2, \zeta_3) \prod_{i=1}^{3} F_1(\zeta_i, t) + \cdots
\end{aligned}
$$

which shows explicitly the successive effects of the binary, ternary$\cdots$ interactions.

I will now leave the formal machinery, and will try to discuss whether the results make sense!

6. Discussion of the kinetic equation. There are a number of requirements which one would expect that the kinetic equation should fulfill.

(a) In the first place one would expect that the first term on the right-hand side of (37) is equivalent to the Boltzmann collision term. I will now show, following Bogoliubov, that this is exactly the case for *spatially uniform systems*.

PROOF. Since in the spatially uniform case F_1 depends only on **p** and t one can omit in $\mathscr{S}_2$ the S_1 operators, and since $S_2(-\tau)$ acting on $\mathbf{p}_1$ or $\mathbf{p}_2$ only involves the relative coordinate $\mathbf{r}_{12} = \mathbf{r}_2 - \mathbf{r}_1$, one easily sees from the first line in (32) that $A^{(1)}$ becomes:

$$(38) \qquad A^{(1)}(\mathbf{p}_1|F_1) = \int d\mathbf{r}_{12} \int d\mathbf{p}_2 \; \Theta_{12} F_1(\mathbf{P}_1^{(2)}, t) F_1(\mathbf{P}_2^{(2)}, t)$$

where:

$$\mathbf{P}_i^{(2)} = \lim_{t \to \infty} S_2(x_1, x_2, -\tau)\mathbf{p}_i, \quad (i = 1, 2)$$

are the constant initial momenta in the binary collision governed by the Hamiltonian H_2 which leads to the phase x_1, x_2 at time zero. The $\mathbf{P}_i^{(2)}$ are functions of $\mathbf{p}_1$, $\mathbf{p}_2$ and $\mathbf{r}_{12}$. Since in terms of the momenta $\mathbf{P}_i^{(2)}$ the Hamiltonian

$$H_2 = \frac{1}{2m}(\mathbf{p}_1^2 + \mathbf{p}_2^2) + \phi_{12} = \frac{1}{2m}\{(\mathbf{P}_1^{(2)})^2 + (\mathbf{P}_2^{(2)})^2\}$$

it follows that:

$$(39) \qquad \{H_2, F_1(\mathbf{P}_1^{(2)}, t) F_1(\mathbf{P}_2^{(2)}, t)\} = 0.$$

This is clearly so if H_2 is expressed in the $\mathbf{P}_i^{(2)}$, but then it also must be so if H_2 is expressed in the original variables x_1, x_2, since the transition from x_1, x_2 to the $\mathbf{P}_i^{(2)}$ is a contact transformation and the Poisson bracket is invariant under such transformations. Written out in the variables x_1, x_2, Eq. (39) implies:

$$\Theta_{12} F_1(\mathbf{P}_1^{(2)}, t) F_1(\mathbf{P}_2^{(2)}, t) = \frac{\mathbf{p}_2 - \mathbf{p}_1}{m} \frac{\partial}{\partial \mathbf{r}_{12}} F_1(\mathbf{P}_1^{(2)}, t) F_1(\mathbf{P}_2^{(2)}, t).$$

Putting this in (38), and using in the $\mathbf{r}_{12}$-integral cylindrical coordinates with the axis in the direction of the relative velocity $\mathbf{g} = (\mathbf{p}_2 - \mathbf{p}_1)/m$, Eq. (38) becomes:

$$(40) \quad A^{(1)}(\mathbf{p}_1|F_1) = \int d\mathbf{p}_2 \int_0^\tau \int_0^{2\pi} gb \, db \, d\varepsilon \int_{-\infty}^{+\infty} dl \frac{\partial}{\partial l} F_1(\mathbf{P}_1^{(2)}, t) F_1(\mathbf{P}_2^{(2)}, t)$$

where l is the coordinate along the cylindrical axis and (b, ε) are the polar coordinates perpendicular to this axis. Clearly the l-integral can be performed. Since at $l \to -\infty$ the two particles are outside

their action sphere and since the $S_2(-\tau)$ will never bring them together:

$$\lim_{l \to -\infty} \mathbf{P}_i^{(2)} = \mathbf{p}_i. \quad (i = 1, 2).$$

On the other hand for $l \to +\infty$, although the particles are then also outside their range of interaction, the $S_2(x_1, x_2, -\tau)$ operation for $\tau \to \infty$ will certainly produce a collision and therefore:

$$\lim_{l \to +\infty} \mathbf{P}_i^{(2)} = \mathbf{p}_i', \quad (i = 1, 2)$$

where the $\mathbf{p}_i'$ are the momenta of the restituting collision $(\mathbf{p}_1', \mathbf{p}_2') \to$ $(\mathbf{p}_1, \mathbf{p}_2)$. Introducing again the differential cross-section $I(g, \theta)$ by:

$$b \, db \, d\varepsilon = I(g, \theta) \, d\Omega$$

(40) becomes:

$$A^{(1)}(\mathbf{p}_1 | F_1) = \int d\mathbf{p}_2 \int d\Omega \, g I(g, \theta) [F_1(\mathbf{p}_1', t) F_1(\mathbf{p}_2', t) - F_1(\mathbf{p}_1, t) F_1(\mathbf{p}_2, t)]$$

which is the Boltzmann collision operator.

For systems which are *not* spatially uniform the proof breaks down and in this case the Boltzmann form of the collision operator can only be an approximation of the $A^{(1)}(x|F_1)$. In a sense this is satisfactory since in the intuitive derivation of the Boltzmann equation it is clear that some uniformity assumptions were really implied. For instance the difference in position of the colliding particles was neglected and it was assumed that the changes of F_1 in time due to the streaming and due to the collisions are strictly additive and do not influence each other. Clearly both these assumptions can only be valid if the spatial variation of F_1 is small, and it is therefore satisfactory that the Bogoliubov theory gives a more general form of the binary collision operator.

(b) The collision terms $A^{(1)}$, $A^{(2)} \cdots$ must have the *cluster-property*, which means that they must be zero if the particles do *not* make a binary, triple $\cdots$ collision. For $A^{(1)}$ this is obvious, because if the two particles stay outside their action sphere then the operator Θ_{12} will make Ω_2 and therefore $A^{(1)}$ zero (see Eq. (33)). For $A^{(2)}$ it can be verified as follows. From Eq. (36) for Ω_3 one sees that the integrand of the x_2-integral will vanish if $|\mathbf{r}_2 - \mathbf{r}_1| > r_0$ because of the Θ_{12} operator. Consequently one needs to consider only those x_2 for which $|\mathbf{r}_2 - \mathbf{r}_1| < r_0$. For this phase (x_1, x_2) the $S_2(1, 2, -\tau)$ operator separates the particles 1 and 2 by a distance r_0 in a time of the

order of the collision time and from that time on the distance of the particles increases. Put:

$$\tilde{x}_i = S_2(1, 2, -\tau)x_i, \quad (i = 1, 2)$$

and call τ' the time for which the distance $|r_2 - r_1|$ has become larger than $2r_0$. The operator occurring in the τ-integral in (36) can now be written as:

(41)
$$\int dx_3 \left[\{\Theta_{13}(\tilde{x}_1, x_3) + \Theta_{23}(\tilde{x}_2, x_3)\}\mathscr{S}_3(\tilde{x}_1, \tilde{x}_2, x_3)\right.$$
$$\left. - \mathscr{S}_2(\tilde{x}_1, \tilde{x}_2)\{\Theta_{13}(\tilde{x}_1, x_3)\mathscr{S}_2(\tilde{x}_1, x_3) + \Theta_{23}(\tilde{x}_2, x_3)\mathscr{S}_2(\tilde{x}_2, x_3)\}\right].$$

For $\tau > \tau'$, $\Theta_{12}(\tilde{x}_1, \tilde{x}_2) = 0$ and for fixed x_3 either $\Theta_{13}(\tilde{x}_1, x_3)$ or $\Theta_{23}(\tilde{x}_2, x_3)$ must be zero, since $\tilde{x}_1$ and $\tilde{x}_2$ are separated by a distance bigger than $2r_0$. Suppose $\Theta_{13}(\tilde{x}_1, x_3) = 0$, but $\Theta_{23}(\tilde{x}_2, x_3) \neq 0$. From the definition of $\mathscr{S}_3$, and since for this configuration $\mathscr{K}_3 = \mathscr{K}_2(\tilde{x}_2, x_3) + \mathscr{K}_1(x_1)$, it is clear that one then has:

$$\mathscr{S}_3(\tilde{x}_1, \tilde{x}_2, x_3) = \mathscr{S}_2(\tilde{x}_2, x_3)$$

and since in this case $\mathscr{S}_2(\tilde{x}_1, \tilde{x}_2) = 1$ one sees that the operator (41) goes to zero. This is also the case if $\Theta_{23}(\tilde{x}_2, x_3) = 0$ but $\Theta_{13}(\tilde{x}_1, x_3) \neq 0$ by a similar argument, and hence one can conclude that Ω_3 is only different from zero if for a time of the order of the collision time the three particles are in a connected configuration.

It would be very valuable if one could further "understand" the expression for Ω_3, in the same way as one "understands" the Boltzmann form of the binary collision operator. For instance one might hope that in the spatially uniform case one could transform Ω_3 in a similar way as Ω_2, so that one would see that Ω_3 depends only on the momenta of the three particles before and after the triple collision. We have not succeeded in doing this and I doubt whether it is possible. However, I still think that it *should* be possible to see so clearly through the structure of the successive collision kernels $\Omega_2, \Omega_3 \cdots$ that one could imagine that with enough insight one would have written them down intuitively just as Boltzmann wrote down his collision term.

(c) One should expect that the kinetic equation will lead to the state of thermodynamic equilibrium and that then F_1 and all the higher distribution functions will agree with the results obtained from the canonical ensemble. It is rather easy to verify that if one takes for F_1 the Maxwell distribution:

(42)
$$F_1^{eq}(x) = (2\pi mkT)^{-3/2} e^{-p^2/2mkT}$$

all the functionals $A^{(1)}(x|F_1^{eq})$ vanish and that then the functionals $F_s(x_1 \cdots x_s|F_1^{eq})$ become the successive terms in the virial expansion of the s-particle equilibrium distribution functions. The simplest is to prove this successively and after a few orders it will then be clear how it goes on.

In zeroth order with (42) $A^{(0)}$ is obviously zero and since F_1^{eq} is spatially uniform one obtains from Eq. (29):

$$F_s^{(0)}(x_1 \cdots x_s|F_1^{eq}) = (2\pi mkT)^{-3s/2} \exp\left\{ - \sum_{i=1}^{s} \frac{(P_i^{(s)})^2}{2mkT} \right\}$$

where:

$$P_i^{(s)} = \lim_{\tau \to \infty} S_s(-\tau)p_i$$

are the momenta of the s particles before the s-tuple collision. Since the Hamiltonian for the s particles can be written as:

$$H_s = \sum_{i=1}^{s} \frac{p_i^2}{2m} + \sum_{i<j} \phi_{ij} = \frac{1}{2m} \sum_{i=1}^{s} (P_i^{(s)})^2 ;$$

one can also write:

$$(43) \qquad F_s^{(0)}(x_1 \cdots x_s|F_1^{eq}) = (2\pi mkT)^{-3s/2} e^{-H_s/kT}$$

which is the expected form for the s-particle distribution function at very low density.

In first order one obtains from (43) and (17b):

$$A^{(1)}(x_1|F_1^{eq}) = (2\pi mkT)^{-3} \int dx_2 \, \Theta_{12} \exp\left(- \frac{p_1^2 + p_2^2}{2mkT} - \frac{\phi_{12}}{kT} \right).$$

Introducing the relative coordinate $r = r_2 - r_1$ the space part of the x_2-integral will be:

$$\int dr \frac{\partial \phi}{\partial r} e^{-\phi/kT}$$

which is clearly zero. Hence $A^{(1)}(x_1|F_1^{eq}) = 0$ as follows of course also from the Boltzmann form for $A^{(1)}$. Since $A^{(1)} = 0$, $D^{(1)}F_s^{(0)} = 0$, and since from (19b) and the definition of $\psi_s^{(1)}$ in (20), restricting ourselves to the case $s = 2$, one has:

$$\psi_2^{(1)}(x_1, x_2|F_1) = -D^{(1)}F_2^{(0)} + \int dx_3(\Theta_{13} + \Theta_{23})F_2^{(0)}$$

one obtains from (30) and (43):

$$(44) \quad F_2^{(1)}(x_1, x_2|F_1^{eq}) = (2\pi mkT)^{-9/2} \int d\tau \, S_2(1, 2, -\tau)$$

$$\times \int dx_3 \, (\Theta_{13} + \Theta_{23}) \, e^{-H_3/kT}.$$

From $\{H_3, \exp(-H_3/kT)\} = 0$ follows:

$$(\Theta_{13} + \Theta_{23})e^{-H_3/kT} = \left(\frac{\mathbf{p}_1}{m}\cdot\frac{\partial}{\partial \mathbf{r}_1} + \frac{\mathbf{p}_2}{m}\cdot\frac{\partial}{\partial \mathbf{r}_2} - \Theta_{12}\right)e^{-H_3/kT} + \frac{\mathbf{p}_3}{m}\cdot\frac{\partial}{\partial \mathbf{r}_3}e^{-H_3/kT}.$$

Introducing this in (44) the last term clearly integrates to zero.   Since:

$$S_2(1, 2, -\tau)\left(\frac{\mathbf{p}_1}{m}\frac{\partial}{\partial \mathbf{r}_1} + \frac{\mathbf{p}_2}{m}\frac{\partial}{\partial \mathbf{r}_2} - \Theta_{12}\right)$$

$$= S_2(1, 2, -\tau)\mathcal{K}_2$$

$$= \mathcal{K}_2 S_2(1, 2, -\tau) = -\frac{d}{d\tau} S_2(1, 2, -\tau)$$

the τ-integral in (44) gives:

$$[1 - S_2(1, 2, -\infty)]e^{-H_3/kT}.$$

Writing $H_3 = H_2 + p_3^2/2m + \phi_{13} + \phi_{23}$ and integrating over $\mathbf{p}_3$, one gets:

$$F_2^{(1)}(x_1, x_2|F_1^{eq})$$

$$= (2\pi mkT)^{-3}[1 - S_2(1, 2, -\infty)]e^{-H_2/kT}\cdot \int d\mathbf{r}_3 \, e^{-(\phi_{13}+\phi_{23})/kT}.$$

Introducing the Mayer function $f_{ij} = \exp(-\phi_{ij}/kT) - 1$, one can write:

$$\int d\mathbf{r}_3 \exp[-(\phi_{13} + \phi_{23})/kT] = \int d\mathbf{r}_3 \, (f_{13}f_{23} + f_{13} + f_{23} + 1).$$

The last three terms are constants, independent of (x_1, x_2), so that $[1 - S_2(1, 2, -\infty)]$ acting on them will give zero.   The first term is a function of $|\mathbf{r}_2 - \mathbf{r}_1|$, which is zero if $|\mathbf{r}_2 - \mathbf{r}_1| > 2r_0$, so that:

$$S_2(1, 2, -\infty) \int d\mathbf{r}_3 f_{13}f_{23} = 0.$$

One obtains therefore:

$$F_2^{(1)}(x_1, x_2|F_1^{eq}) = (2\pi mkT)^{-3} e^{-H_2/kT} \int d\mathbf{r}_3 f_{13}f_{23}$$

(45)

$$= F_2^{(0)}(x_1, x_2|F_1^{eq}) \int d\mathbf{r}_3 f_{13}f_{23}$$

which is the familiar expression as derived from the canonical distribution.[4] By the same argument as used for $A^{(1)}$ it follows from (45) and (17c) that $A^{(2)}(x_1|F_1^{eq}) = 0$, and so on!

(d) We have shown therefore that the equilibrium distributions are solutions of the Bogoliubov equations. Are these solutions always reached in time? Or in other words, can one generalize Boltzmann's *H*-theorem? Unfortunately there is here a gap in the theory. So far we have been unable to do this. I feel sure that it *must* be possible but one is hampered by the lack of insight in the structure of the successive collision kernels so that it is difficult to see how one should generalize the argument of Boltzmann.

7. Remarks on the theory of the hydrodynamical stage. It would take much too long to explain in detail the further work of Dr. S. T. Choh on the generalization of the Chapman-Enskog development to the kinetic equation of Bogoliubov. Let me therefore only point out what is involved and indicate how far the theory has progressed.

The first step is again the derivation of the *general macroscopic equations*. Since these equations are exact consequences of the BBGKY hierarchy, and since it may be useful to have them somewhere together I will still write them out in detail, and to facilitate the comparison with the analogous development in §2 of Chapter VI I will use in parallel with $F_1, F_2, \cdots$ the distribution functions $f_1(\mathbf{r}, \mathbf{v}, t)$, $f_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{v}_1, \mathbf{v}_2, t)$ in the velocities instead of in the momenta. The connection between them is given by:

$$f_1(\mathbf{r}, \mathbf{v}, t)\, d\mathbf{v} = \frac{N}{V}\, F_1(\mathbf{r}, \mathbf{p}, t)\, d\mathbf{p},$$

(46)

$$f_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{v}_1, \mathbf{v}_2, t)\, d\mathbf{v}_1\, d\mathbf{v}_2 = \frac{N(N-1)}{V^2}\, F_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{p}_1, \mathbf{p}_2, t)\, d\mathbf{p}_1\, d\mathbf{p}_2$$

and so on.

The macroscopic quantities, which describe the macroscopic state of the gas, are:

(a) the mass density $\rho = nm$, where:

$$n(\mathbf{r}, t) = \int d\mathbf{v}\, f_1(\mathbf{r}, \mathbf{v}, t);$$

(b) the average flow velocity $\mathbf{u}(\mathbf{r}, t)$, defined by:

$$nu_i(\mathbf{r}, t) = \int d\mathbf{v}\, v_i f_1(\mathbf{r}, \mathbf{v}, t);$$

(c) the internal energy density $\varepsilon(\mathbf{r}, t)$, which consists of two parts:

$$(47) \qquad \varepsilon(\mathbf{r}, t) = \varepsilon^{\text{kin}}(\mathbf{r}, t) + \varepsilon^{\text{pot}}(\mathbf{r}, t)$$

where:

$$(47a) \qquad \varepsilon^{\text{kin}} = \frac{1}{2} m \int d\mathbf{v} \; U^2 f_1(\mathbf{r}, \mathbf{v}, t)$$

with $U_i = v_i - u_i = $ thermal velocity (note that ε^{kin} was called Q in Chapter VI), and where:

$$(47b) \qquad \varepsilon^{\text{pot}} = \frac{1}{2} \int d\mathbf{v} \int d\mathbf{v}_1 \int d\mathbf{r}_1 \; \phi(|\mathbf{r} - \mathbf{r}_1|) f_2(\mathbf{r}, \mathbf{r}_1, \mathbf{v}, \mathbf{v}_1, t).$$

In terms of these five quantities one obtains from the BBGKY hierarchy the macroscopic equations in exactly the same form as in Chapter VI, namely:

$$(48) \begin{cases} \text{(a)} & \dfrac{\partial \rho}{\partial t} + \dfrac{\partial}{\partial x_\alpha}(\rho u_\alpha) = 0, \\[2ex] \text{(b)} & \rho \dfrac{Du_i}{Dt} = -\dfrac{\partial P_{i\alpha}}{\partial x_\alpha}, \\[2ex] \text{(c)} & \rho \dfrac{D}{Dt}\left(\dfrac{\varepsilon}{\rho}\right) + \dfrac{\partial q_\alpha}{\partial x_\alpha} = -P_{\alpha\beta}D_{\alpha\beta} \end{cases}$$

with:

$$\frac{D}{Dt} \equiv \frac{\partial}{\partial t} + u_\alpha \frac{\partial}{\partial x_\alpha}; \qquad D_{ij} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right).$$

However now the pressure tensor P_{ij} and the heat current density q_i consist just as the energy density ε out of two parts, a kinetic part and a part which depends on the intermolecular potential ϕ. One finds:

$$(49) \qquad P_{ij} = P_{ij}^{\text{kin}} + P_{ij}^{\text{pot}}$$

where P_{ij}^{kin} is defined just as in Chapter VI by:

$$(49a) \qquad P_{ij}^{\text{kin}}(\mathbf{r}, t) = m \int d\mathbf{v} \; U_i U_j f_1(\mathbf{r}, \mathbf{v}, t)$$

and where:

$$(49b) \qquad P_{ij}^{\text{pot}}(\mathbf{r}, t) = -\frac{1}{2} \int d\boldsymbol{\rho} \; \frac{\rho_i \rho_j}{\rho^2} \frac{d\phi}{d\rho} \int_0^\rho d\lambda \; n_2(\mathbf{r}_1, \mathbf{r}_2, t).$$

Here $n_2(\mathbf{r}_1, \mathbf{r}_2, t)$ is the pair density distribution defined by:

$$(50) \qquad n_2(\mathbf{r}_1, \mathbf{r}_2, t) = \int\int d\mathbf{v}_1 \, d\mathbf{v}_2 f_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{v}_1, \mathbf{v}_2, t)$$

and the positions $\mathbf{r}_1$, $\mathbf{r}_2$ are related to $\mathbf{r}$, and the relative coordinate $\boldsymbol{\rho} = \mathbf{r}_2 - \mathbf{r}_1$ by:

$$(51) \qquad \mathbf{r}_1 = \mathbf{r} + (\lambda - \rho)\frac{\boldsymbol{\rho}}{\rho}, \qquad \mathbf{r}_2 = \mathbf{r} + \lambda\frac{\boldsymbol{\rho}}{\rho}.$$

Finally one has:

$$(52) \qquad q_i = q_i^{\text{kin}} + q_i^{\text{pot}}$$

where again q_i^{kin} is defined just as in Chapter VI by:

$$(52a) \qquad q_i^{\text{kin}}(\mathbf{r}, t) = \frac{1}{2}m \int d\mathbf{v} \, U_i U^2 f_1(\mathbf{r}, \mathbf{v}, t)$$

and where:

$$
(52b) \qquad
\begin{aligned}
q_i^{\text{pot}}(\mathbf{r}, t) = {} & \frac{1}{2}\int d\mathbf{r}_1 \int\int d\mathbf{v} \, d\mathbf{v}_1 \, U_{1i}\phi(|\mathbf{r} - \mathbf{r}_1|)f_2(\mathbf{r}, \mathbf{r}_1, \mathbf{v}, \mathbf{v}_1, t) \\
& + \frac{1}{4}\int d\boldsymbol{\rho}\, \frac{\rho_i \rho_\alpha}{\rho^2}\frac{d\phi}{d\rho}\int_0^\rho d\lambda \int\int d\mathbf{v}_1 \, d\mathbf{v}_2 (U_{1,\alpha} + U_{2,\alpha})f_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{v}_1, \mathbf{v}_2, t).
\end{aligned}
$$

In the second line the positions $\mathbf{r}_1$, $\mathbf{r}_2$ are again expressed in $\mathbf{r}$ and $\boldsymbol{\rho}$ by (51), and

$$\mathbf{U}_i = \mathbf{v}_i - \mathbf{u}, \quad (i = 1, 2).$$

In note 5 we indicate some of the rather straightforward manipulations required to derive (48) from the BBGKY equations. It is also not difficult to give a physical interpretation of the potential energy parts in P_{ij} and q_i, but we will leave this to the reader.

One now has to use the expressions the Bogoliubov theory gives for the second distribution function F_2 in terms of F_1, and then just as in Eq. (21) of Chapter VI one must develop F_1 in an uniformity parameter θ, postulating at the same time hydrodynamical equations of the form:

$$(53) \qquad
\begin{aligned}
\frac{\partial n}{\partial t} &= \theta N^{(1)} + \theta^2 N^{(2)} + \cdots, \\[1mm]
\frac{\partial u_i}{\partial t} &= \theta V_i^{(1)} + \theta^2 V_i^{(2)} + \cdots, \\[1mm]
\frac{\partial \varepsilon}{\partial t} &= \theta E^{(1)} + \theta^2 E^{(2)} + \cdots
\end{aligned}
$$

where the $N^{(1)}$, $V^{(1)}$ and $E^{(1)}$ are functions of the position r and depend on the time only through their functional dependence on the macroscopic variables n, u and ε.

Unfortunately the formulas become rather involved, and for all details I have to refer to the dissertation of Dr. S. T. Choh. In conclusion let me therefore only state what Dr. Choh has been able to show.

1. In first order of θ one gets the ideal or Euler hydrodynamical equations, in which the pressure p as function of T and ρ is given by the usual (equilibrium) virial expansion and where the internal energy ε is given by the corresponding thermal equation of state.

2. In second order of θ one gets the Navier-Stokes equations, or in other words one obtains Fourier's law of heat conduction:

$$q_i = -\kappa \frac{\partial T}{\partial x_i}$$

and Newton's law of internal friction:

$$P_{ij} = p\delta_{ij} - 2\mu_1\left(D_{ij} - \frac{1}{3}\delta_{ij}D_{\alpha\alpha}\right) - \mu_2 D_{\alpha\alpha}\delta_{ij}$$

which now involves *two* viscosity coefficients.

3. For the transport coefficients μ_1, μ_2 and κ one gets virial expansions of the expected form (2), but unfortunately the actual values of the expansion coefficients depend on the solution of inhomogeneous integral equations of the same form as occur in the Chapman-Enskog theory but much more complicated since the inhomogeneous part now involves the three particle streaming operator. One can show that these equations have an unique solution, but to *find* the solution even for special intermolecular potentials (like the elastic sphere or the Maxwell model) seems very complicated, so that no numerical results have been obtained so far.

Notes on Chapter VII

1. The work of N. N. Bogoliubov was published in his book: *Problemy Dinamicheskoi Teorii v Statisticheskoi Fisike* (Moscow, 1946). An excerpt in English appeared in J. Phys. (U.S.S.R.) **10** (1946) 265, and a complete translation (by E. K. Gora) appears in the first volume of the "Studies in Statistical Mechanics" (North Holland Publishing Co., Amsterdam, 1962). A short account of the theory was presented by one of us at the Boulder Summer Seminar in 1957 and this was published as Appendix 1 in the book by M. Kac (*Probability and Related Topics in the Physical Sciences*, Interscience, New York, 1958). Further consequences of the Bogoliubov theory have been worked out in the University of Michigan dissertations of S. T. Choh (*The Kinetic Theory of Phenomena in Dense Gases*, 1958) and of R. L. Guernsey (*The Kinetic Theory of Fully Ionized Gases*, 1960). In the text we follow mainly the exposition by S. T. Choh.

The work of J. G. Kirkwood has appeared in a series of papers in J. Chem. Phys. See especially: J. Chem. Phys. **14** (1946) 180 and **15** (1947) 72. Compare also the account given by J. G. Kirkwood and J. Ross in the Proceedings of the International Symposium on Transport Processes in Statistical Mechanics (Interscience, New York, 1958). In these proceedings one also finds a paper by M. S. Green, which is a summary of his article in the J. Chem. Phys. **25** (1956) 836. More recent work of the same author appeared in Physica **24** (1958) 393 and in Vol. III of the 1960 Boulder Lectures in Theoretical Physics (Interscience, New York, 1961).

The work of Prigogine and co-workers appeared in a series of papers in Physica since 1956. Some of the recent ones are by I. Prigogine and R. Balescu, Physica **25** (1959) 281, 302, 324; **26** (1960) 145, 529. Compare also the application to the kinetic theory of plasmas by R. Balescu (Phys. Fluids **3** (1960) 52).

A useful comparison of the different methods of deriving the Boltzmann equation has been made by E. G. D. Cohen (Physica **27** (1961) 163). In here one finds also further references.

Finally one should point out that the *first* attempt of a kinetic theory of dense gases was made by D. Enskog (Kungl. Svenska Vet. Akad. Handl. **63**, No. 4 (1921); see also Chapman and Cowling, *Mathematical*

Theory of Non-uniform Gases, Chapter 16). Enskog always used the hard sphere model and he started from the Boltzmann equation in which the collision term was modified by taking into account the difference of position of the two colliding molecules at the moment of impact and by assuming that the influence of the other molecules can be accounted for by changing the collision probability by a factor

(a)
$$\chi = 1 + \frac{5}{8}\frac{b}{v}$$

where b is the van der Waals' b, which insures that in equilibrium the equation of state is correct up to and including the third virial coefficient. To this modified Boltzmann equation the Chapman-Enskog development can be applied and this leads to a virial expansion of the transport coefficients of the form (2). In fact one finds:

(b)
$$\frac{\mu}{\mu_0} = 1 + \frac{7}{40}\frac{b}{v} + \cdots,$$

$$\frac{\kappa}{\kappa_0} = 1 + \frac{23}{40}\frac{b}{v} + \cdots.$$

The Enskog theory has been discussed by many authors; see for instance: H. B. Hollinger and C. F. Curtiss, J. Chem. Phys. **33** (1960) 1386 and J. V. Sengers and E. G. D. Cohen, Physica **27** (1961) 230, where one finds also further references. There is no doubt that the Enskog theory explains at least qualitatively what happens at higher densities. However, because of the lack of a systematic procedure and especially because of the uncertain validity of the Ansatz (a), it is at present *not* known whether the numerical coefficients in the virial expansions (b) are correct.

2. For the derivations by Bogoliubov and by Kirkwood see the references in Note 1. The work of M. Born and H. S. Green appeared in a series of papers in the Proceedings of the Royal Society. They are collected in a book called *A General Kinetic Theory of Fluids* (Cambridge University Press, Cambridge, 1949). For the work of J. Yvon see his monograph *La Théorie Statistiques des Fluids* in the Actualités Scientifiques et Industrielles (Hermann, Paris, no. 203, 1935).

3. The fact that the application of a boundary condition like (26) but for $\tau \to -\infty$ leads to the wrong sign in the collision term of the Boltzmann equation, was pointed out by E. G. D. Cohen and T. H. Berlin (Physica **26** (1960) 717). In this paper and also in the article

by E. G. D. Cohen (Physica **27** (1961) 163) it was pointed out that in *all* derivations of the Boltzmann equation from the Liouville equation a similar choice of the appropriate solution is made.

Clearly a further clarification of the role of the boundary condition (26) can come about only when one sees in which way the solution of the initial value problem for the Liouville equation reaches the form (14) postulated by Bogoliubov. We hope and we expect that this insight will come from the work of M. S. Green.

4. See J. E. Mayer and E. Montroll, J. Chem. Phys. **9** (1941) 2, where one finds the general expressions for the $F_s^{(1)}(x_1 \cdots x_s | F_1^{eq})$. For a discussion of the virial expansion of the s-particle distribution function with the help of the theory of linear graphs as in Chapter II see the review article of the authors quoted in Note 6 of Chapter II.

5. We will follow essentially the work of J. H. Irving and J. G. Kirkwood, J. Chem. Phys. **18** (1950) 817. The method is completely analogous to the method used in Chapter VI to derive the macroscopic equations from the Boltzmann equation.

Start from the first equation (11a) of the BBGKY hierarchy. Integrating over p_1 leads immediately to the continuity equation (48a) since the right-hand side vanishes. Multiplying (11a) by p_1/m and integrating over p_1, one obtains after some simple transformations:

$$\text{(c)} \quad \rho \frac{Du_i}{Dt} = -\frac{\partial P_{i\alpha}^{kin}}{\partial x_\alpha} - \int d\mathbf{r}_1 \int d\mathbf{v} \int d\mathbf{v}_1 \frac{\partial \phi(|\mathbf{r} - \mathbf{r}_1|)}{\partial x_i} f_2(\mathbf{r}, \mathbf{r}_1, \mathbf{v}, \mathbf{v}_1, t)$$

where we have changed to velocity variables and the distribution f_2 according to (46). The question remains to show that the last term in (c) can be written as the divergence of the second part P_{ij}^{pot} of the pressure tensor. The simplest way is to verify. From (49b) one gets:

$$\frac{\partial P_{i\alpha}^{pot}}{\partial x_\alpha} = -\frac{1}{2} \int d\mathbf{\rho} \frac{\rho_i \rho_\alpha}{\rho^2} \frac{d\phi}{d\rho} \int_0^\rho d\lambda \frac{\partial}{\partial x_\alpha} n_2(\mathbf{r}_1, \mathbf{r}_2, t).$$

Since n_2 is a function of $\mathbf{r} + \lambda \mathbf{\rho}/\rho$ and ρ (see Eq. (51) defining $\mathbf{r}_1$ and $\mathbf{r}_2$), it is clear that:

$$\frac{\partial n_2}{\partial \lambda} = \frac{\rho_\alpha}{\rho} \frac{\partial n_2}{\partial x_\alpha}.$$

Hence:

$$\frac{\partial P_{i\alpha}^{pot}}{\partial x_\alpha} = -\frac{1}{2} \int d\mathbf{\rho} \frac{\rho_i}{\rho} \frac{d\phi}{d\rho} \{n_2(\mathbf{r}, \mathbf{r} + \mathbf{\rho}, t) - n_2(\mathbf{r} - \mathbf{\rho}, \mathbf{r}, t)\}.$$

Changing in the second term the direction of $\boldsymbol{\rho}$, and using the symmetry of n_2 in the position variables, one gets:

$$\frac{\partial P_{\beta\alpha}^{\text{pot}}}{\partial x_\alpha} = -\int d\boldsymbol{\rho}\, \frac{\rho_i}{\rho}\frac{d\phi}{d\rho}\, n_2(\mathbf{r}, \mathbf{r} + \boldsymbol{\rho}, t)$$

and this is identical with the last term in (c) if there one puts $\mathbf{r}_1 = \mathbf{r} + \boldsymbol{\rho}$.

To derive the energy equation (48c) one multiplies (11a) by $p_1^2/2m$ and integrates over $\mathbf{p}_1$. Using (48b) one then obtains:

(d)
$$\rho\frac{D}{Dt}\left(\frac{\varepsilon^{\text{kin}}}{\rho}\right) + \frac{\partial q_\alpha^{\text{kin}}}{\partial x_\alpha} = -P_{\alpha\beta}D_{\alpha\beta} + \frac{\partial}{\partial x_\alpha}(u_\beta P_{\alpha\beta}^{\text{pot}})$$
$$- \int d\mathbf{r}_1 \iint d\mathbf{v}\, d\mathbf{v}_1\, v_\alpha\, \frac{\partial\phi(|\mathbf{r} - \mathbf{r}_1|)}{\partial x_\alpha} f_2(\mathbf{r}, \mathbf{r}_1, \mathbf{v}, \mathbf{v}_1, t).$$

To obtain the transport equation of the potential energy density we have to use the second equation (11b) of the BBGKY hierarchy. By multiplying (11b) with $\phi(|\mathbf{r}_1 - \mathbf{r}_2|)/2$ and by integrating over $\mathbf{r}_2$, $\mathbf{p}_1$ and $\mathbf{p}_2$ one obtains after some rearrangements and renamings and after changing to velocity variables:

(e)
$$\rho\frac{D}{Dt}\left(\frac{\varepsilon^{\text{pot}}}{\rho}\right) + \frac{\partial q_\alpha^{\text{pot}(1)}}{\partial x_\alpha}$$
$$= \frac{1}{2}\int d\mathbf{r}_1 \iint d\mathbf{v}\, d\mathbf{v}_1 (v_\alpha - v_{1,\alpha})\frac{\partial\phi(|\mathbf{r} - \mathbf{r}_1|)}{\partial x_\alpha} f_2(\mathbf{r}, \mathbf{r}_1, \mathbf{v}, \mathbf{v}_1, t)$$

where $q_i^{\text{pot}(1)}$ is the first part of the potential energy part of the heat current density given by the first line in Eq. (52b). Adding equations (d) and (e), and using the expression (49b) for P_{ij}^{pot}, one gets:

$$\rho\frac{D}{Dt}\left(\frac{\varepsilon}{\rho}\right) + \frac{\partial}{\partial x_\alpha}(q_\alpha^{\text{kin}} + q_\alpha^{\text{pot}(1)}) = -P_{\alpha\beta}D_{\alpha\beta}$$
$$- \frac{1}{2}\int d\mathbf{r}_1 \iint d\mathbf{v}\, d\mathbf{v}_1\, \frac{\partial\phi(|\mathbf{r} - \mathbf{r}_1|)}{\partial x_\alpha}(U_\alpha + U_{1,\alpha})f_2(\mathbf{r}, \mathbf{r}_1, \mathbf{v}, \mathbf{v}_1, t).$$

Finally it is easy to verify that the last term is the divergence of the second part of q_i^{pot} given by the second line in Eq. (52b), which concludes the proof of the energy equation.

Quantum Statistics of Interacting Particles

By Elliott W. Montroll

1. The partition function. As was pointed out in the lectures of Professor Uhlenbeck, the calculation of thermodynamic properties of an assembly of particles can be accomplished by performing appropriate elementary operations (taking logarithms, differentiation, etc.) on the *partition function*. In the case of an assembly whose dynamics is described by the laws of quantum mechanics, this function is

$$(1) \qquad Z = \sum_j \exp - \beta E_j$$

where the set $\{E_j\}$ is the set of all energy levels of the assembly; i.e. the set of characteristic values of the Schrödinger equation

$$(2) \qquad H\psi_j = E_j\psi_j,$$

the H being the Hamiltonian operator of the assembly and the ψ_j's the wave functions or characteristic functions of H. The parameter β is $1/kT$, T being the temperature of the assembly and k Boltzmann's constant.

Clearly, if one can solve the Schrödinger equation for the assembly of interest, the calculation of Z is trivial. Generally, ψ is a function of $3N$ (with $N = 0\,(10^{23})$ being the number of particles in our assembly) variables, say the position vectors of the particles in the assembly, and H is an operator which depends on the same variables. If one postulates additivity of intermolecular forces, then

$$(3a) \qquad H = -\frac{\hbar^2}{2m} \sum_{j=1}^{N} \nabla_j^2 + \sum_{k>j}^{N} \sum_{j=1}^{N-1} \phi(r^{jk})$$

where

$$(3b) \qquad \nabla_j^2 = \frac{\partial^2}{\partial x_j^2} + \frac{\partial^2}{\partial y_j^2} + \frac{\partial^2}{\partial z_j^2}$$

and $\phi(r^{ij})$ is the potential energy of interaction between the ith and jth particles when they are separated by a distance r^{ij}. The only interesting case of interacting particles for which the Schrödinger equation has been solved exactly is that of coupled harmonic oscillators (crystals undergoing small vibrations). For all other significant examples, approximations must be made. My lectures are concerned with the systematic application of perturbation theory to the problem of the calculation of the partition function. Although a considerable part of the discussion will be quite general, the example which I hope to analyze in some detail is that of the gas of ionized particles. In that case ϕ represents the coulomb interaction

$$(4) \qquad \phi(r^{ij}) = \frac{e_i e_j}{r^{ij}},$$

e_j being the charge on the jth particle.

The methods presented in the lectures are those developed by J. C. Ward and myself. They are closely connected with those developed independently by Matsubara; Huang, Lee, and Yang; Bloch and DiDominicis; Gell-Mann and Brueckner; Goldstone, and other authors. The characteristic feature of all this work is that perturbation theory is developed in a systematic way and that diagrams are used extensively. These techniques were inspired by the celebrated paper of Feynman on the theory of electrons and positrons. As the development proceeds, I suspect that occasionally you mathematicians will be amused by the methods, but probably the recklessness of the approach will more often give you a feeling of uneasiness. A proper mathematical investigation of the expansion of the partition function into a series of divergent cluster integrals and their recollection into convergent expressions would be most welcome.

Actually, Martin and Schwinger, Fradkin, Siegert and others have discussed the partition function by nonperturbative techniques but these lead to the necessity of making other types of approximation. Their approach will not be discussed here but it might be of interest to some of you.

The partition function (1) can be written in an alternative form in terms of the characteristic functions $\{\psi_j\}$ of (2). Each ψ depends on the schematic variable

$$(5) \qquad r \equiv \{r^1, r^2, \cdots, r^N\}.$$

Then

$$(6) \qquad Z = \int \cdots_V \int \sum_j \psi_j^*(r)\psi_j(r)e^{-\beta E_j} \, d^{3N}r = \text{trace exp} - \beta H.$$

Note that the operator exp $-\beta H$ plays a decisive role in equilibrium statistical mechanics while exp $itH/\hbar$ is the operator from which dynamics can be developed. That is, the real part of the complex variable $\beta + it\hbar^{-1}$ is associated with thermodynamics and the imaginary part with dynamics while both the real and imaginary parts find their place in the statistical mechanics of nonequilibrium processes. We start our development with an analyses of Boltzmann statistics. In the case of fermions or bosons the summation over j in (6) and (7) is taken over only antisymmetric or symmetric ψ's.

We define what is technically known as a "propagator" by

$$K(2, 1) \equiv K(r_2\beta_2; r_1\beta_1) = \begin{cases} \sum_j e^{-(\beta_2-\beta_1)E_j}\psi_j^*(r_1)\psi_j(r_2) & \text{if } \beta_2 \geqq \beta_1 \\ 0 & \text{if } \beta_2 < \beta_1 \end{cases}$$

(7)

$$= \theta(\beta_2 - \beta_1) \sum_j e^{-(\beta_2-\beta_1)E_j} \psi_j^*(r_1)\psi_j(r_2)$$

$\theta(x)$ being the Heaviside step function

$$\theta(x) = \begin{cases} 1 & \text{if } x \geqq 0 \\ 0 & \text{if } x < 0. \end{cases}$$

(8)

$$d\theta/dx = \delta(x).$$

(9)

The partition function is then

$$Z = \int \cdots \int_V K(r\beta; r0)\, d^{3N}r.$$

(10)

Although the case $\beta_2 < \beta_1$ does not appear directly in this formula, the setting of $K \equiv 0$ under this condition will be convenient in the perturbation theory of the calculation of Z since certain restricted integrations over β's will be replaced by unrestricted ones. Actually, an extra factor $1/N!$ should be introduced into (10) because in integrating freely over the r's, many sets of possible positions differ from each other only through a permutation of particles so that they are overcounted by a factor $N!$. In §§ 1 and 2 lower indices on r's identify the value of β with which the r is associated; i.e. r_2 is the r value (Eq. 5) at β_2. The upper indices denote particle numbers.

Since

$$\sum_j \psi_j^*(r_1)\psi_j(r_2) = \delta(r_2 - r_1),$$

(11)

$$H(2)\psi_j(r_2) = E_j\psi_j(r_2), \quad \text{and} \quad \partial\theta(x)/\partial x = \delta(x)$$

(12)

where $H(2)$ is the Hamiltonian operator in terms of the variables

(13)
$$r_2 = \{r_2^1, r_2^2, \cdots, r_2^N\},$$

we have

(14)
$$\left(\frac{\partial}{\partial \beta_2} + H(2)\right)K(2, 1) = \delta(\beta_2 - \beta_1)\, \delta(r_2 - r_1).$$

This equation is just the Green's function form of the Schrödinger equation with β replaced by $it/\hbar$. The homogeneous form of this equation is often called the Bloch equation. The propagator is a Green's function.

In the case of free particles, the Hamiltonian is

(15)
$$H_0(2) = -\hbar^2 \sum_j \nabla_j^2/2m$$

and (14) is just the point source diffusion equation for N independent particles with a diffusion constant $D = \hbar^2/2m$. In all cases

$$\delta(r_2 - r_1) = \prod_{j=1}^{N} \delta(r_2^j - r_1^j).$$

The free particle propagator, which is the solution of

(16)
$$\left\{\frac{\partial}{\partial \beta_2} + H_0(2)\right\}K_0(2, 1) = \delta(\beta_2 - \beta_1)\, \delta(r_2 - r_1),$$

is then

(17)
$$K_0(2, 1) = \theta(\beta_2 - \beta_1) \prod_{j=1}^{N} K_0^j(2, 1)$$

where $K_0^j(2, 1)$ has two equivalent forms in the case of an unbounded space

(18)
$$K_0^j(2, 1) = \frac{1}{(2\pi h)^3} \int \exp\{ip^j \cdot (r_2^j - r_1^j)h^{-1} - \frac{1}{2m}(\beta_2 - \beta_1)(p^j)^2\}\, d^3p^j$$

(19)
$$\equiv \frac{\exp - \{m(r_2^j - r_1^j)^2/2\hbar^2(\beta_2 - \beta_1)\}}{[2\pi\hbar^2(\beta_2 - \beta_1)/m]^{3/2}}.$$

The form for K_0^j in a finite cubic box of volume $L^3 = V$ with periodic boundary conditions is

(20)
$$\frac{V}{(2\pi h)^3} \sum_{p_1 p_2} \delta_{p_1, p_2} \left(\frac{2\pi h}{L}\right)^6$$
$$\times \exp[i(p_2^j \cdot r_2^j - p_1^j \cdot r_1^j)/\hbar - (\beta_2 - \beta_1)(p_1^j)^2/2m]$$

where the summation proceeds over all momentum states

(21) $$p = \frac{2\pi n \hbar}{L}, \quad n = 0, \pm 1, \pm 2, \cdots$$

and δ_{p_1, p_2} is a Kronecker delta.   As $L \to \infty$ we write

(22) $$d^3 p = (2\pi\hbar/L)^3$$

so that the summation becomes a double integral.   The fact that

(23) $$\delta(p_2 - p_1) = \lim_{V \to \infty} \frac{V \delta_{p_1 p_2}}{(2\pi\hbar)^3}$$

implies that (20) reduces to (18) in the required limit.

2. Perturbation theory.   With a knowledge of K_0, we are prepared to give a systematic perturbation theory of K.   Let

$$H = H_0 + H_I$$

where H_0 is given by (15).   Then the differential equation (14) is equivalent to the integral equation

(24) $$K(2, 1) = K_0(2, 1) - \int_V \int_{-\infty}^{\infty} K_0(2, 3) H_I(3) K(3, 1) \, d^{3N} r_3 \, d\beta_3.$$

This equivalence can be verified by applying the operator $(\partial/\partial\beta_2 + H(2))$ to obtain (in view of (16) and (24))

$$\left(\frac{\partial}{\partial\beta_2} + H(2)\right) K(2, 1) = H_I(2) K_0(2, 1) + \delta(\beta_2 - \beta_1) \, \delta(r_2 - r_1)$$

$$- H_I(2) \int_V \int_{-\infty}^{\infty} K_0(2, 3) H_I(3) K(2, 1) \, d^{3N} r_3$$

$$- \int_V \int_{-\infty}^{\infty} \delta(\beta_2 - \beta_3) \, \delta(r_2 - r_3)$$

$$\times H_I(3) K(3, 1) \, d^{3N} r_3 \, d\beta_3$$

$$= H_I(2) K_0(2, 1) + \delta(\beta_2 - \beta_1) \, \delta(r_2 - r_1)$$

$$- H_I(2) K(2, 1) + H_I(2)[K(2, 1) - K_0(2, 1)]$$

$$= \delta(\beta_2 - \beta_1) \, \delta(r_2 - r_1)$$

as is required.   Since both $K_0(2, 1)$ and $K(2, 1)$ were defined to vanish when $\beta_2 < \beta_1$, the limits on (24) could just as well be written as going from β_1 to β_2 so that (24) is equivalent to

(25) $$K(2, 1) = K_0(2, 1) - \int_V \int_{\beta_1}^{\beta_2} K_0(2, 3) H_I(3) K(3, 1) \, d^{3N} r_3 \, d\beta_3.$$

This equation can be integrated to yield

(26) $K(2, 1) = K_0(2, 1) - \int_V \int_{\beta_1}^{\beta_2} K_0(2, 3) H_I(3) K_0(3, 1)\, d^{3N}r_3\, d\beta_3 +$

$\int_V \int_{\beta_1}^{\beta_2} \int_V \int_{\beta_1}^{\beta_3} K_0(2, 3) H_I(3) K_0(3, 4) H_I(4) K_0(4, 1)\, d^{3N}r_4\, d\beta_4\, d^{3N}r_3\, d\beta_3 - \cdots.$

If H_I is proportional to a coupling constant λ, this expansion is a power series in λ and therefore a perturbation series. If we use the explicit formula for H_I given in (3a)

(27) $H_I(3) = \sum_{k>j}^{N} \sum_{j=1}^{N-1} \phi(r_3^j, r_3^k)$

and at first restrict ourselves to the case $N = 3$

$$H_I(3) = \phi(r_3^1, r_3^2) + \phi(r_3^1, r_3^3) + \phi(r_3^2, r_3^3)$$

then (26) becomes

(28) $K(2, 1) = K_0(2, 1) - \int_V \int_{\beta_1}^{\beta_2} K_0(2, 3)[\phi(r_3^3, r_3^1) + \phi(r_3^1, r_3^2)$

$+ \phi(r_3^2, r_3^3)] K_0(3, 1)\, d^{3N}r_3\, d\beta_3 + (9 \text{ second order terms}) \cdots.$

Each term in this expansion can be identified by a Feynman type diagram in β, r space. The factor in $K_0(2, 1)$ which represents particle "1" being propagated as a free particle from β_1 to β_2 (see Eq. (19) for analytical form)
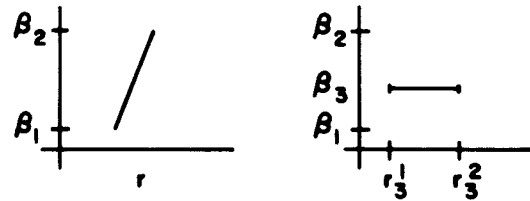
Figure 1

is represented by a line from level β_1 to level β_2, while the interaction $\phi(r_3^1, r_3^2)$ at β_3 is represented by the horizontal line in Fig. 1. The zero order term has the diagram given in Fig. 2 while three parts

contribute to the first order term.   These are given in Fig. 3.

Figure 2

(a)   (b)   (c)
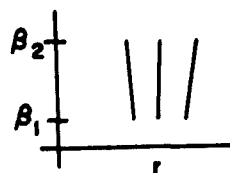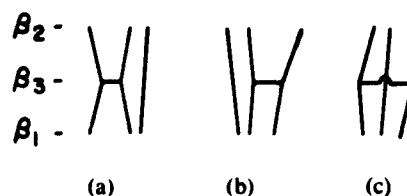
Figure 3

Of the nine terms of second order, three are drawn in Fig. 4.   These are obtained by inserting one more interaction line at β_4 with $(\beta_4 < \beta_3)$.

(a_1) (a_2) (a_3)
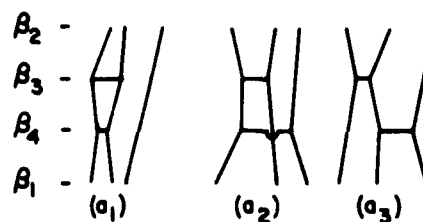
Figure 4

Three more terms can be obtained from (b) in this way as can three from (c).   Higher order terms are obtained in a similar manner.   It is to be emphasized that all interaction lines are "isothermal," both ends existing at the same temperature (β values).

In the partition function we must set $\beta_1 = 0$, $\beta_2 = \beta$, $r_1 = r_2 = r$ and integrate over r.   Then

$$(29) \quad Z = \frac{1}{3!}\left\{\int_V K_0(r\beta, r0)\, d^9r - \int_V \int_V d^9r\, d^9r_3\right.$$
$$\left. \times \int_0^\beta d\beta_3 K_0(r\beta, r_3, \beta_3) \sum \phi(r_3^j - r_3^k) K_0(r_3\beta_3; r0) + \cdots\right\}.$$

All diagrams of the partition function extend over the β range $(0, \beta)$ and all diagrams start and end at the same r values.   All points on the strip in (β, r) space which correspond to the range $(0, \beta)$ can be mapped on a cylinder of circumference β, and in view of the identity of the r values at each end of the range all our particle lines form closed curves on the cylinder.   When periodic boundary conditions are applied, the cylinder becomes a torus.   We represent our diagrams by the form they have on the cylinder.   The free particles of Fig. 5 have the representation

$$O \quad O \quad O \quad : \text{free particles.}$$
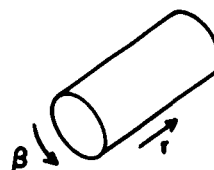
Figure 5

The terms of first and second order in (29) correspond to the diagrams

$$\text{QO } O \;+\; \text{QOO} \;+\; O \text{ QO} \quad : \text{one interaction}$$

$$\text{QO } O \;+\; \text{QOO} \;+\; \text{QOO} \;+\; 6 \text{ similar terms: two interactions}$$

Note that in a term of (29) in which two particles are connected by interaction lines and one remains free, the appropriate integral factors into two parts, one a triple integral over the free particle position coordinates and the other a six-fold integral over the position co-ordinates of the interacting pair.

Generally, in the case of an assembly of N interacting particles,

$$(30) \quad Z_N = \frac{1}{N!}\left\{\int_V K_0(r\beta:r0)\, d^{3N}r - \int\int_V d^{3N}r\, d^{3N}r_3\right.$$
$$\left. \times \int_0^\beta K_0(r\beta:r_3\beta_3) \sum_{j>k} \phi(r_3^j - r_3^k) K_0(r_3\beta_3:r0)\, d\beta_3 + \cdots\right\}.$$

A typical integral in the expansion might correspond to a diagram with s_1 free particles, s_2 pairs of particles connected by interaction lines, s_3 triples connected by interaction lines, etc.   Then that integral factors into s_1 factors of integrals of individual particle positions; s_2 factors of integrals over positions of pairs of particles, etc.   Of course, any integral associated with a diagram which corresponds to l connected particles appears as a factor in many terms in the expansion of the partition function Z.
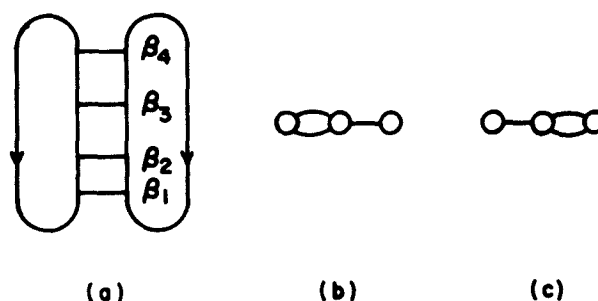
Figure 6

Now let us consider the sum b_l of all integrals which correspond to diagrams of l particles connected by any number of interaction lines $n \geq l - 1$:

(31) $b_l = \dfrac{1}{l!} \sum$ (integral associated with a diagram of l connected particles)

   $\times$ (number of ways diagram can be constructed from l particles).

A remark or two is appropriate about the integrals.   These were first defined so that the interaction lines occur in an appropriate sequence

(32) $0 < \beta_1 < \beta_2 < \cdots \beta_k < \beta.$

In a very symmetric diagram such as that given in Fig. 6, one might wish to integrate freely over all β's instead of adhering to the conditions (32).   Then he would have to divide by $k!$ because an interchange of the β_k's does not change the character of the diagram.   These interchanges can be made in $k!$ ways.   Also consider the two diagrams 6b and 6c.   These would be recorded in b_3 as a single diagram because in the r and β integrations of Fig. 6b, one automatically arrives at a diagram which is topologically also of the form of Fig. 6c.

The quantity b_l contains all possible connected diagrams with l points, each diagram being given its appropriate weight. Some examples are

$$b_1 = 0,$$

(33) $$b_2 = \frac{1}{2} \; \text{O—O} \; + \frac{1}{4} \; \text{O≠O} \; + \frac{1}{12} \; \text{O≡O} \; + \cdots,$$

$$b_3 = \frac{1}{2} \; \text{O—O—O} \; + \frac{1}{6} \; \triangle \; + \cdots.$$

There is a one-to-one correspondence between every term in (30) and every term in

(34) $$Z_N = \sum \prod_{\Sigma l s_l = N} b_l^{s_l}/s_l!.$$

The factor $N!/s_1! s_2! \cdots$ is the number of ways N particles can be divided into subsets such that s_1 subsets contain one particle, s_2 two particles, etc. The summation in (34) extends over all partitions of N such that

(34a) $$\sum l s_l = N.$$

The grand partition function of a grand canonical ensemble of systems composed of any number of particles of our type of interest

(35) $$Z_G = \sum_{N=1}^{\infty} z^N Z_N.$$

This equation, when combined with (34) yields

(36) $$Z_G = \sum_{N=1}^{\infty} \sum \prod_{\Sigma l s_l = N} (z^l b_l)^{s_l}/l! = \exp \sum b_l z^l$$

so that

(37) $$\log Z_G = \sum b_l z^l.$$

The logarithm of the grand partition function is then the sum over all *connected* diagrams containing any number of particles; a factor z^l weights any diagram composed of l particles.

Let us now investigate the influence of quantum statistics on the calculation of the b_l's. Quantum statistics is a consequence of the indistinguishability of particles of the same species. Two diagrams exist which correspond to a pair of particles starting at (r^1, r^2) and ending at the same points. Both are exhibited in Fig. 7. An observer

who makes observations at $\beta = 0$ and β cannot distinguish between the two cases; both must be included in the evaluation of the partition function.

When Fig. 7b is mapped on a cylinder in (r, β) space particle 1 ends where 2 starts (Fig. 7d) and vice versa so that (7b) is equivalent to a single particle which circulates around our (r, β) cylinder twice, or in the case of periodic boundary conditions around our (r, β) torus twice. This discussion of indistinguishability can be generalized immediately to sets of any number of particles. A set of n particles such that 1 ends where 2 started, 2 ends where 3 started, $\cdots$, n ends

(a)   (b)   (c)
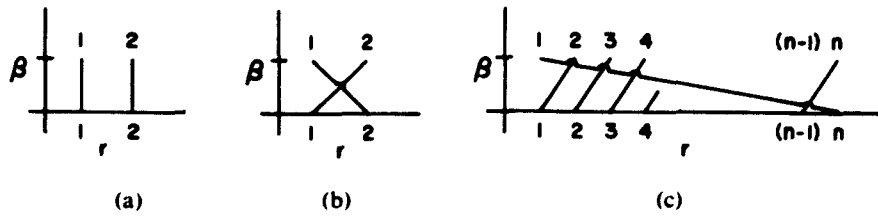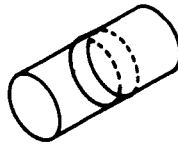
Figure 7

Figure 7d   Figure 7e

where 1 started (see Fig. 6c) maps on the (r, β) cylinder or torus as one particle which circulates around n times, the total length of β space spanned being $n\beta$. We call such a construct an n-toron. Should our particles be fermic ·s, a factor (-1) must be included for each particle interchange between $\beta = 0$ and $\beta = \beta$. This is a consequence of the definition of the propagator K (see Eq. 7). In the case of fermions the summation over wave functions ψ, in (7) is restricted to extend only over the antisymmetric wave functions of the operator H. Hence the interchange in the position of two particle coordinates in one of the ψ_j's results in a change in sign. If at $\beta = \beta_1$ in Eq. (7) the jth wave function is $\psi_j(r_1^1, r_1^2, \cdots)$ and if at $\beta = \beta_2$ two r_2's are

exchanged, the resulting $\psi_j(r_2)$ changes sign as does $K(2, 1)$. Indeed when $(n - 1)$ exchanges in sign occur as in Fig. 6c (an n-toron) one must include a factor $(-1)^{n-1} = (-1)^{n+1}$ with the free particle propagator. No (-1) factors appear in assemblies of bosons because in that case the summation in (7) extends only over symmetrical wave functions ψ_j.

In the case of N free fermions a typical set of interchanges of initial coordinates r_1 at β_1 to final coordinates r_2 at β_2 can be represented by a diagram similar to that in Fig. 8. The set of all possible inter-
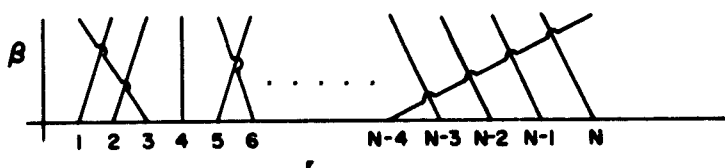
Figure 8

changes (with appropriate signs) can be generated by the Nth order determinant

$$(38) \quad K_0^{(N)}(r_2\beta_2; r_1\beta_1) = \frac{1}{N!} \det_N \{K_0(r_2^j\beta_2; r_1^k\beta_1)\} \equiv \frac{1}{N!} \det (2, 1)$$

where the element in the jth row and kth column is just the free particle propagator (19) which takes a particle from (r_1^k, β_1) to (r_2^j, β_2) (i.e. the function obtained by replacing r_1^j in (19) by r_1^k. This determinant has the required antisymmetry with respect to the exchange of two initial coordinates or two final coordinates since such an exchange is equivalent to exchanging a pair of rows or columns in the determinant. The symmetrical boson propagator is $(N!)^{-1}$ multiplied by the permanent of $K_0(r_2^j\beta_2; r_1^k\beta_1)$.

The propagator of a set of N interacting fermions is obtained from (26) by replacing $K_0(2, 1)$ by $(1/N!) \det (2, 1)$ and all the $K_0(2, 3)$ by $(1/N!) \det (2, 3)$. The resulting fermion propagator

$$(39) \quad K^F(2, 1) = \frac{1}{N!} \left[\det (2, 1) - \int_V \int_{\beta_1}^{\beta_3} \det (2, 3) H_i(3) K_0(3, 1) \, dr_3 \, d\beta_3 \right.$$

$$\left. + \int_V \int_{\beta_1}^{\beta_3} \det (2, 3) H_i(3) K_0(3, 4) H_i(4) K_0(4, 1) \, dr_4 \, d\beta_4 \, dr_3 \, d\beta_3 - \cdots \right].$$

The antisymmetry of $K^F(2, 1)$ with respect to interchange of the final

r's follows from the fact that the final coordinates only appear in the determinant factors. The antisymmetry with respect to exchange of initial coordinates is clear from the following argument when $H_I(3)$ is symmetrical with respect to interchange of pairs of initial particle coordinates. Exchange two particle coordinates in r_1, say r_1^1, and r_1^2 in the second term in (39). The term $K_0(3, 1)$ has the same form as it would without the interchange if we replace r_3^1 by r_3^2 and r_3^2 by r_3^1. This does not change the volume element for integration or the inter-action part of the Hamiltonian $H_I(3)$ (provided that $H_I(3)$ is sym-metrical in all particle variables). It, however, does interchange a pair of columns in the determinant so that the determinant can only be returned to its original form at the expense of changing the sign of the second term in (39). The same argument can be applied to each term in the perturbation expansion.

The fermion partition function is then

$$(40) \quad Z_N^F = \frac{1}{N!} \left[\int \det (1, 1) \, dr_1 \right.$$
$$\left. - \int \cdots \int \det (1, 3) H_I(3) K_0(3, 1) \, dr_3 \, d\beta_3 \, dr_1 + \cdots \right].$$

As in the Boltzmann case the partition function can be expanded as a sum of products of integrals over connected clusters or subsets of particles. However, now clusters can exist even in the absence of interactions; the n-toron is a cluster of n particles which are connected by virtue of their indistinguishability. In the case of bosons the determinants in (40) are to be replaced by permanents.

If one introduces an extended b_l which is the $(1/l!)$ multiplied by the sum over all integrals which correspond to diagrams of l particles connected by any number of interaction lines or by indistinguish-ability or both, one can rederive (34), or with the introduction of the grand partition function (37). The first few b_l's are now

$$b_1 = 0,$$

$$(41) \quad b_2 = \frac{1}{2} \, \text{⟨⟩} + \frac{1}{2} \, \text{O-O} + \text{⟨⟩} + \frac{1}{4} \, \text{O=O} + \cdots,$$

$$b_3 = \frac{1}{3} \, \text{⟨⟩} + \frac{1}{2} \, \text{O-O-O} + \text{O-⟨⟩} + \frac{1}{6} \, \triangle + \cdots.$$

Here ① represents a 2-toron, ⑳ a 3-toron, etc.

The next section contains a derivation of the set of rules needed for the calculation of each component of a b_l.

3. Algorithm for construction of integrals associated with diagrams. The form we use for the free particle propagator is (18)

$$(42) \quad K_0(r_2\beta_2; r_1\beta_1) = \frac{1}{(2\pi h)^3} \int \exp\left[i(r_2 - r_1)\cdot ph^{-1} - \frac{1}{2m}(\beta_2 - \beta_1)p^2\right] d^3p$$

and the form we use for the potential energy of interaction is its Fourier integral representation

$$(43) \qquad \phi(r_2 - r_1) = \int u(q) \exp[iq\cdot(r_2 - r_1)h^{-1}] d^3q.$$

Although considerable generality exists in our development, the example which we frequently have in mind in our discussions is the coulomb interaction

$$(44) \qquad\qquad \phi(r) = e^2/r$$

(e being the charge on any one of our particles). It is easily verified that the appropriate form for $u(q)$ is

$$(45) \qquad\qquad u(q) = e^2/2h\pi^2q^2$$

since

$$(46) \qquad \frac{1}{r} = \int \frac{1}{2h\pi^2q^2} \exp(iq\cdot rh^{-1}) d^3q.$$

In this example our perturbation theory is an expansion in powers of e^2.

In the absence of any interaction the only contribution to b_l is an l-toron or a free particle which encircles our (r, β) cylinder l times, thus spanning a range $l\beta$ of β space in its course which starts and ends at the same point r. The appropriate integrand for b_l is (since $\beta_2 - \beta_1 = l\beta$ in (40) while $r_2 = r_1 = r$)

$$(47a) \qquad K_0(r, l\beta; r, 0) = \frac{1}{(2\pi h)^3} \int \exp(-l\beta p^2)/2m \, d^3p,$$

which is independent of r. We must finally integrate this over all possible starting positions r. This integration merely contributes the volume of the container since (47) is independent of r. In the case of fermions a factor $(-1)^{l+1}$ must be added. Hence

$$b_l = \frac{1}{l!} \left\{ \frac{V(-1)^{l+1}}{(2\pi h)^3} \int \exp(-l\beta p^2)/2m \, d^3p \right\}$$

$\times$ {number of ways an l-toron can be constructed from l particles}.

The ordering of our l particle lines, each of length β, around our (r, β) cylinder is equivalent to that of l points connected in a ring. The number of different ways this can be done is $(l - 1)!$ Hence

$$(47b) \qquad b_l = \frac{(\mp 1)^{l+1}}{l} \frac{V}{(2\pi\hbar)^3} \int \exp\left(-l\beta p^2/2m\right) d^3p,$$

the upper sign being appropriate for fermions and the lower for bosons.

The grand partition function and hence (PV/kT) of a set of free fermions or bosons is obtained by substituting (47b) into (37).   One obtains the well-known result

$$(48) \quad PV/kT = \log Z_G = \mp \frac{V}{(2\pi\hbar)^3} \sum_l l^{-1} \int \left(\mp z \exp -\beta p^2/2m\right)^l d^3p$$

$$= \pm \frac{V}{(2\pi\hbar)^3} \int \log\left(1 \pm z\, e^{-\beta p^2/2m}\right) d^3p$$

The parameter z must be chosen so that

$$(49) \qquad \rho = \frac{N}{V} = \frac{Z}{V} \frac{\partial \log Z_G}{\partial z}$$

$$= \frac{1}{(2\pi\hbar)^3} \int \frac{z \exp\left(-\beta p^2/2m\right) d^3p}{1 \pm z \exp\left(-\beta p^2/2m\right)}$$

is the preassigned density of our assembly.

We begin our discussion of the influence of interactions by considering the most elementary diagram fragment with an interaction, a free particle line connected with a single interaction line (Fig. 9).
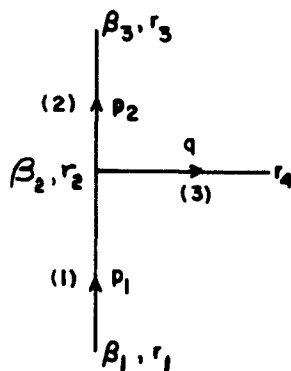
Figure 9

When such a fragment exists as part of a more complicated cluster integral, the contribution to $\log Z_G$ involves the integration over all points at which interactions can occur. Hence one would have to integrate in particular over all values of r_2. At fixed r_2 the propagator of our fragment is the product of propagators (1), (2), and (3):

$$(50a) \quad (1) \quad \frac{1}{(2\pi\hbar)^3} \int \exp\left[i(r_2 - r_1)\cdot p_1\hbar^{-1} - (\beta_2 - \beta_1)p_1^2/2m\right] d^3p_1,$$

$$(50b) \quad (3) \quad -\int u(q) \exp\left[iq\cdot(r_4 - r_2)\hbar^{-1}\right] d^3q,$$

$$(50c) \quad (2) \quad \frac{1}{(2\pi\hbar)^3} \int \exp\left[i(r_3 - r_2)\cdot p_2\hbar^{-1} - (\beta_3 - \beta_2)p_2^2/2m\right] d^3p_2.$$

The minus sign appears in (3) because in the basic integral equation (25) the interaction $H_I(3)$ appears with a minus sign so that in all iterations which occur in the perturbation theory the minus sign always goes with H_I and therefore with $u(q)$. If we multiply these three together and integrate over all r_2, this integration yields a factor

$$(51) \quad \int \exp\left[ir_2\cdot(p_1 - q - p_2)\hbar^{-1}\right] d^3r_2 = (2\pi\hbar)^3 \delta(p_1 - q - p_2).$$

The variable p_1 represents the momentum of our free particle while it goes from r_1 to r_2, p_2 that is in the transition from r_2 to r_3 while q is the momentum transferred from r_2 to r_4 due to the interaction of our particle of interest at r_2 with another at r_4. Eq. (51) is just a statement of the conservation of momentum at $(r_2\beta_2)$:

$$(52) \quad\quad\quad\quad\quad\quad p_1 = p_2 + q.$$

One must also integrate over all possible values of β_2 at which an interaction might take place. This is most conveniently accomplished through the introduction of an energy variable s which is conjugate to β in a manner analogous to that in which p and r are conjugate. We note that

$$(53) \quad\quad S(\alpha; p) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{e^{is\alpha}\, ds}{is + p^2/2m} = \begin{cases} e^{-\alpha p^2/2m} & \text{if } \alpha > 0, \\ 0 & \text{if } \alpha < 0. \end{cases}$$

This representation is especially useful because it allows one to integrate freely over the various β variables. For example, suppose interactions were to occur at β_1 and β_3 in Fig. 9 as well as at β_2, so that if the inequality $\beta_1 < \beta_2 < \beta_3$ were violated, the complete graph

of which Fig. 9 is a fragment would change its shape.   Through use of a representation similar to (53) for the Gaussian in (1) and (2) one would be able to integrate freely on β_2 from $-\infty$ to $+\infty$ because the integral would vanish automatically when β_2 extended beyond its allowed range (β_1, β_3).

We are now in a position to derive general rules for the construction of the integral associated with an arbitrary diagram such as that given in Fig. 10.   We do this by first finding a simple expression for
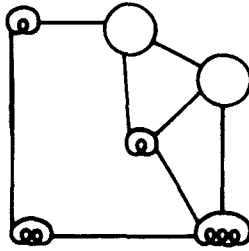
Figure 10

a single toron fragment of such a diagram.   Then we find rules for combining torons.   Fig. 11 represents a typical N toron with n interaction lines at

$$(54) \qquad 0 < \beta_1 < \beta_2 < \cdots < \beta_n < N\beta.$$

The momentum transfer at these points is

$$q_1, q_2, \cdots, q_n.$$

Our N-toron has been mapped into a circle of circumference $N\beta$, the first turn when constructed on our (r, β) cylinder is included in the range $(0, \beta)$, the second turn in the range $(\beta, 2\beta)$, etc.   We denote the full propagator associated with the fragment in Fig. 11 by

$$(55) \qquad F_N(r_1'r_2'\cdots; \beta_1'\beta_2'\cdots).$$

The translational and periodic symmetry of a toron is such that a translation of all interaction points by an amount β leads to exactly the original diagram again.   This would weight the same diagram twice.   In order to avoid such a multiple weighting, we restrict the interaction β_1 to the interval $(0, \beta)$

$$(56) \qquad 0 < \beta_1 < \beta.$$
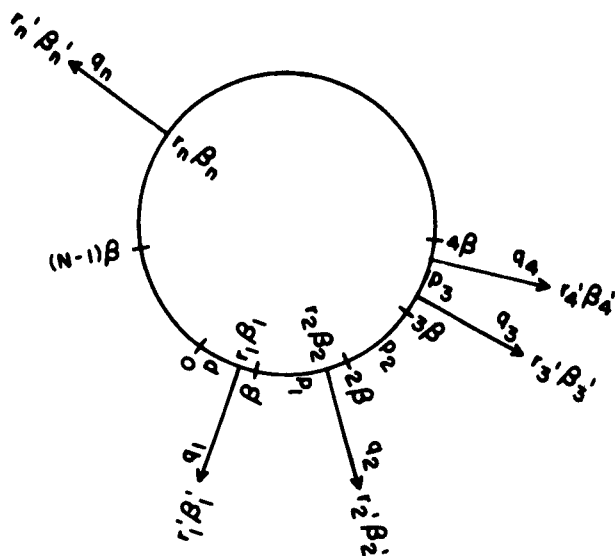
Figure 11

Now our propagator (55) is the product of

(a) all free particle propagators which carry particles from β_1 to β_2, β_2 to β_3, etc. (r_0 and β_0 being identified with r_n and β_n)

(57) $\qquad \prod_{j=1}^{n} \left\{ (2\pi h)^{-3} \int \exp \left[i(r_j - r_{j-1}) \cdot p_j h^{-1} - (\beta_j - \beta_{j-1}) p_j^2 / 2m \right] d^3 p_j \right\};$

(b) all interaction propagators

(58) $\qquad \prod_{j=1}^{n} \int \left[-u(q_j) \right] \exp \left[iq_j \cdot (r_j' - r_j) h^{-1} \right] d^3 q_j;$

(c) $(-1)^{N+1}$ for fermions;

(d) z^N, a weight z being associated with each particle when one calculates $\sum b_l z^l$.

One must finally integrate over all points (r_j, β_j) at which interactions can occur on our N-torons. We have denoted the momentum of a free particle between the jth and $(j + 1)$st interactions by p_j. It is convenient to define the momentum p by

(59) $\qquad\qquad\qquad p \equiv p_n.$

It is exactly the momentum of the free particle which exists at $\beta = 0$.

We begin our calculation of $F_N(r'_1, \cdots, \beta'_n)$ by examining all the terms in the product of (a), (b), (c), and (d) which contain only r_1, $r_2, \cdots, r_n$. Integrating over r_j and applying the results (51) and (52) we find that the $(2\pi h)^{-3}$ factors in (57) cancel out and the momentum conservation laws

(60a) $$p_{j-1} = p_j + q_j, \qquad j = 2, 3, \cdots, n,$$

(60b) $$p_n = p_1 + q_1,$$

also appear through delta functions similar to that in (51). Each p_j can be expressed in terms of p (see (59)) and the q's through

(61) $$p_j = p + q_{j+1} + q_{j+2} + \cdots + q_n, \qquad j < n.$$

If we add all terms in (60a) and (60b) we find

(62) $$q_1 + q_2 + \cdots + q_n = 0.$$

This is just a statement that the total momentum leaving our N-toron through interactions is zero as one would have expected.

We summarize the above results by collecting all the factors which now contribute to (55) with the exception of the β_j dependent factors of (57). The only remaining independent free particle momentum variable is p; the rest disappearing through the integration over the delta functions which led to (60). The condition (62) is expressed by introducing a delta function factor $\delta(q_1 + - + q_n)$ into our expression for F_N. Our required expression is

(63) $$-(-z)^N \int \cdots \int d^3p \, d^3q_1 \cdots d^3q_n \, \delta(q_1 + q_2 + - + q_n)$$

$$\times \prod_{j=1}^{n} [-u(q_j) \exp(iq_j \cdot r'_j h^{-1})] \, (\beta \text{ dependent factor}).$$

We finish our calculation of F_N by examining the β dependent factor of (63). It is the β integral under the restrictions (54) and (56). The β dependent factors of (63) are just those of (57), namely the Gaussian factors. In order to simplify the β integrations we use the representation (53), for then we can integrate freely over the β's with the restriction (54) removed with the assurance that when it is violated the integrand will vanish automatically. Our required factor before

integration is then (the S function being defined by (53))

(64) $\quad S(\beta_2 - \beta_1; p_1)S(\beta_3 - \beta_2; p_2)\cdots S(\beta_n - \beta_{n-1}; p_{n-1})$

$$\times \; S(N\beta - (\beta_n - \beta_1); p_n) = \int \delta(N\beta + \beta_1 - \beta_{n+1})\, d\beta_{n+1}$$

$$\times \prod_{j=1}^{n} S(\beta_{j+1} - \beta_j; p_j)$$

where β_{n+1} is defined to be

(65) $$\beta_{n+1} = N\beta + \beta_1.$$

We have postulated the interaction with other torons to occur at β values $\beta_1', \beta_2', \cdots, \beta_n'$. Since all interactions are isothermal β_j must correspond to the same temperature as β_j'. All levels $\beta_j', \beta_j' + \beta$, $\beta_j' + 2\beta, \cdots$, etc., are at the same temperature on our (r, β) cylinder and our isothermal condition can be expressed as

(66) $$\beta_j' = \beta_j \bmod \beta, \qquad j = 1, 2, \cdots, n.$$

The delta function of period β

(67) $$\delta_\beta(\beta_j' - \beta_j) = \frac{1}{\beta} \sum_{t_j = -\infty}^{\infty} e^{2\pi i t_j (\beta_j' - \beta_j)/\beta}$$

vanishes unless $\beta_j' = \beta_j \bmod \beta$. On the other hand

(68) $$\int_0^\beta \delta_\beta(\beta_j' - \beta_j)\, d\beta_j = 1.$$

If a factor $\delta_\beta(\beta_j' - \beta_j)$ is introduced into (64) for each j, then the resulting quantity will vanish unless each β_j has a value compatible with the preassigned β_j''s. Our expression of interest is then

(69) $$\int \delta(N\beta + \beta_1 - \beta_{n+1})\, d\beta_{n+1} \prod_{j=1}^{n} \delta_\beta(\beta_j' - \beta_j)S(\beta_{j+1} - \beta_j; p_j).$$

Furthermore, in the calculation of a cluster integral one must integrate over all possible points at which interactions can occur; i.e. over all $\beta_{j-1} < \beta_j < \beta_{j+1}$. Since our S function was defined to vanish when $\beta_{j+1} < \beta_j$ for all j, we can integrate freely on (69) except for β_1, which (see 56) was limited to the range $(0, \beta)$

(70) $$\int_0^\beta \cdot d\beta_1 \int_{-\infty}^{\infty} \cdots \int \delta(N\beta + \beta_1 - \beta_{n+1})\, d\beta_{n+1}\, d\beta_n \cdots d\beta_1$$

$$\times \prod_{j=1}^{n} \delta_\beta(\beta_j' - \beta_j)S(\beta_{j+1} - \beta_j; p_j).$$

Following (53) we set $(j = 1, 2 \cdots n)$

$$(71) \qquad S(\beta_{j+1} - \beta_j; p_j) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{\exp i(\beta_{j+1} - \beta_j)s_j}{is_j + p_j^2/2m} \, ds_j.$$

After substituting (71), (67) and the Fourier integral representation of the first delta function of (69),

$$(72) \qquad \delta(N\beta + \beta_1 - \beta_{n+1}) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i(N\beta + \beta_1 - \beta_{n+1})s_{n+1}} \, ds_{n+1},$$

into (69), it becomes

$$(73) \quad \frac{1}{2\pi\beta^n} \sum_{t_1 \cdots t_n = -\infty}^{\infty} \int_{-\infty}^{\infty} \cdots \int e^{iN\beta s_{n+1}} \, ds_1 \cdots ds_{n+1}$$

$$\times \prod_1^n \left\{ \left[\frac{p_j^2}{2m} + is_j \right]^{-1} \exp 2\pi i t_j \beta_j'/\beta \right\} \int_0^\beta d\beta_1 \exp \left\{ i\beta_1 \left(s_{n+1} - s_1 - \frac{2\pi t_1}{\beta} \right) \right\}$$

$$\times \prod_{j=2}^{n+1} \left\{ \frac{1}{2\pi} \int_{-\pi}^{\pi} d\beta_j \exp i\beta_j (s_{j-1} - s_j - \frac{2\pi t_j}{\beta}) \right\}$$

where $t_{n+1} \equiv 0$. The integral with respect to β_j is exactly

$$(74) \qquad \delta\left(s_{j-1} - s_j - \frac{2\pi t_j}{\beta} \right).$$

Hence we have the energy conservation law

$$(75a) \qquad s_{j-1} = s_j + 2\pi t_j/\beta, \qquad j = 2, \cdots, n,$$

$$(75b) \qquad s_{n+1} = s_n,$$

at each interaction point. This is analogous to the momentum conservation (60) except that the quanta of energy transferred are multiples of $(2\pi/\beta)$ since t_j is always an integer. We define s by

$$(76) \qquad s \equiv s_n = s_{n+1}.$$

If we sum over j in (75) we find

$$(77) \qquad \frac{2\pi}{\beta} (t_2 + \cdots + t_n) = s_1 - s_n = s_1 - s_{n+1}$$

so that

$$(78) \qquad s_{n+1} - s_1 - \frac{2\pi t_1}{\beta} = \frac{2\pi}{\beta} \sum_1^n t_j.$$

Hence the β_1 integral is equivalent to

$$(79) \qquad \int_0^\beta d\beta_1 \exp \left(\frac{2\pi i\beta_1}{\beta} \sum_1^n t_j \right) = \beta \, \delta_{t_1 + t_2 + \cdots + t_n, 0}.$$

The s integrations are carried out successively with the aid of (69) and (70) starting with s_{n-1} and ending with s_1.   Expression (73) reduces to

$$(80) \quad \frac{1}{2\pi\beta^{n-1}} \sum_{t_1, \cdots, t_n = -\infty}^{\infty} \delta_{t_1 + \cdots + t_n, 0} \int_{-\infty}^{\infty} ds \, e^{is\beta N}$$

$$\times \prod_{j=1}^{n} \left\{ e^{2\pi i t_j \beta_j'/\beta} \left[\frac{p_j^2}{2m} + is_j \right]^{-1} \right\}$$

where

$$(81a) \qquad\qquad s_j = s + \frac{2\pi}{\beta}(t_{j+1} + \cdots + t_n), \qquad j < n,$$

$$(81b) \qquad\qquad s_n \equiv s, \qquad p \equiv p_n,$$

and the other p's are related to p and the q's by (61). Eq. (80) is just the β dependent factor which must be inserted into (63).

At this stage it should be noted that one can very well collect a complete class of fragments of diagrams together; namely, all those which are torons similar to Fig. 11 with n interaction lines.   If we insert (80) into (63) and sum over all N from 1 to ∞, we find a single expression

$$(82) \quad F(r_1', r_2' \cdots ; \beta_1', \beta_2' \cdots \beta_n') = \sum_{N=1}^{\infty} F_N(r_1', \cdots, \beta_n')$$

$$= \sum_{t_1 \cdots t_2 = -\infty}^{\infty} \int \cdots \int d^3q_1 \cdots d^3q_n \beta^{1-n} \delta(q_1 + \cdots + q_n) \delta_{t_1 + \cdots + t_n, 0}$$

$$\times A_n(q_1 t_1, \cdots, q_n t_n) \prod_{j=1}^{n} \{-u(q_j) \exp i[q_j \cdot r_j h^{-1} + 2\pi t_j \beta_j'/\beta]\}$$

where

$$(83) \quad A_n(q_1 t_1 \cdots q_n t_n) = \frac{1}{2\pi} \int \cdots \int d^3p \, ds \, w(is) \prod_{j=1}^{n} \left\{ is_j + \frac{p_j^2}{2m} \right\}^{-1}$$

and

$$(84) \qquad w(is) = \begin{cases} ze^{i\beta s}/(1 + ze^{i\beta s}) & \text{Fermi Dirac,} \\ ze^{i\beta s}/(1 - ze^{i\beta s}) & \text{Einstein Bose,} \\ ze^{i\beta s} & \text{Maxwell Boltzmann.} \end{cases}$$

The Fermi Dirac form of $w(is)$ follows immediately from (63) and (82).   The Einstein Bose case follows after the minus signs are removed from the term in front of the integral sign in (63).   The Maxwell Boltzmann result corresponds to the case $N = 1$ in (63), since in this classical limit only torons of order one occur.

Let us now direct ourselves to the problem of combining fragments such as Fig. 11 to yield complete cluster integrals. The free particle

(a)   (b)
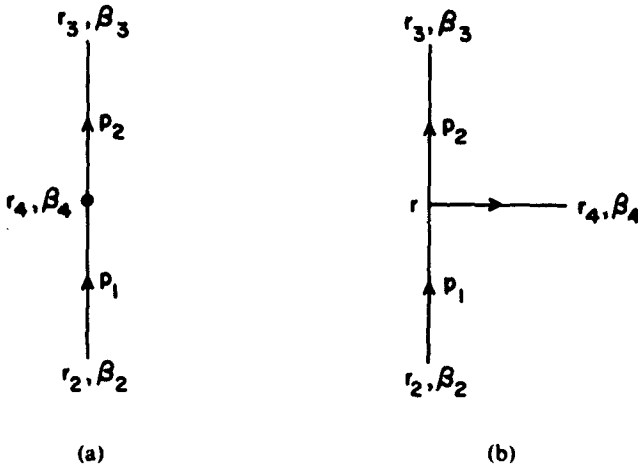
Figure 12

propagator which has three fixed positions (Fig. 12a) differs from the propagator of a fragment with three fixed positions, one at the end of an interaction line (Fig. 12b) by having the interaction propagator

$$u(p_2 - p_1)$$

replaced by

$$(2\pi h)^{-3}.$$

This follows from the fact that the integrations over r in (12b) yields a factor $(2\pi h)^3$ (see Eq. 51) which would not appear in (12a). The interaction line of (12b) of course does not appear in (12a).

Now suppose that in a general fragment such as that in Fig. 11, an interaction line is omitted and an unintegrated point is left on the toron. Then the appropriate $u(q)$ in (82) would be replaced by $(2\pi h)^{-3}$.

To get a feel for what is involved in combining fragments to produce complete cluster integrals, we start by combining the two fragments (a) and (b) of Fig. 13 by integrating over the connecting point $(r_2\beta_2)$.
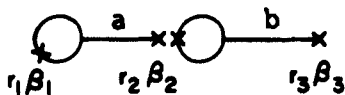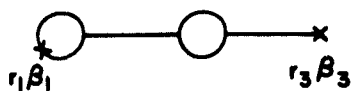
Figure 13   Figure 14

The propagators of fragments (a) and (b) are respectively

$$\beta^{-1} \sum_{t_1 t_2} \int \int d^3q_1 d^3q_2\, \delta(q_1 + q_2)\Lambda_2(q_1 t_1; q_2 t_2)[-u(q_2)](2\pi\hbar)^{-3}$$

$$\exp i[(q_1 \cdot r_1 + q_2 \cdot r_2)\hbar^{-1} + 2\pi(t_1\beta_1 + t_2\beta_2)/\beta]$$

$$= \beta^{-1} \sum_{t_2} \int d^3q_2\, \Lambda_2(-q_2, -t_2; q_2 t_2)[-u(q_2)](2\pi\hbar)^{-3}$$

$$\times \exp i[q_2 \cdot (r_2 - r_1)\hbar^{-1} + 2\pi t_2(\beta_2 - \beta_1)/\beta]$$

and

$$\beta^{-1} \sum_{t_2'} \int d^3q_2'\, \Lambda_2(-q_2', -t_2'; q_2' t_2')[-u(q_2')](2\pi\hbar)^{-3}$$

$$\times \exp i[q_2' \cdot (r_3 - r_2)\hbar^{-1} + 2\pi t_2'(\beta_3 - \beta_2)/\beta].$$

If we multiply these two propagators together and integrate over r_2 and β_2, we obtain

$$(85) \quad \frac{1}{\beta(2\pi\hbar)^3} \sum_{t_2} \int d^3q_2\, \Lambda_2^2(-q_2, -t_2; q_2, t_2)[-u(q_2)]^2$$

$$\times \exp i[q_2 \cdot (r_3 - r_1)\hbar^{-1} + 2\pi t_2(\beta_3 - \beta_1)/\beta].$$

One can proceed in the same manner to show that a chain of n torons (Fig. 15a) has a propagator

$$(86) \quad \mathcal{F}^n(r'', \beta''; r', \beta') = \frac{1}{\beta(2\pi\hbar)^3} \sum_t \int d^3q\, \Lambda_2^n(-q, -t; q, t)[-u(q)]^n$$

$$\times \exp i[q \cdot (r'' - r')\hbar^{-1} + 2\pi t(\beta'' - \beta')/\beta].$$
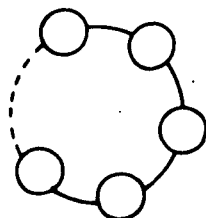
(a)   (b)

Figure 15

The propagator of a ring of n particles is obtained by letting $r'' \equiv r'$, $\beta'' \equiv \beta'$ and integrating over all r' vectors which are in our container of volume V as well as over all β' in the range $(0, \beta)$. We then obtain

$$(87) \qquad \frac{V}{(2\pi h)^3} \sum_t \int d^3q \{ -\Lambda_2(-q, -t:q, t)u(q) \}^n.$$

A combinatorial factor is also associated with the ring diagram. This is $1/n!$ multiplied by the number of ways a ring of n objects can be formed from n objects, $(n - 1)!$, the number already discussed in connection with a free n-toron. The required combinatorial factor is actually $(1/2)(n - 1)!/n! = 1/2n$. The factor $1/2$ arises because in the calculation of the number of possible rings every ordering of particles occurs as well as the corresponding reverse ordering while in the integration over all possible momentum transfers q around the ring both signs of q, $+$ and $-$ occur. The $-q$ momentum transfer in a given ring ordering is equivalent to the $+q$ momentum transfer in the reverse ordering. Hence the factor $1/2$ must be inserted to compensate for this overcounting of a configuration by a factor of 2.

The sum over all rings is (counting $\mathbf{O\!\!=\!\!O}$ as a ring of two torons):

$$(88) \quad \text{Sum over all rings} = \frac{V}{2(2\pi h)^3} \sum_t \int d^3q$$

$$\sum_{n=2}^{\infty} [-u(q)\Lambda_2(-q_1, -t:q, t)]^n/n$$

$$= \frac{V}{2(2\pi h)^3} \sum_t \int d^3q \{ \Lambda_2(-q, -t:q, t)u(q)$$

$$- \log [1 + u(q)\Lambda_2(-q, -t:q, t)] \}.$$

The simplest diagrams with one toron acting as a node are given in Fig. 16. Both of these are composed of two chains and one toron with four interaction points. In Fig. 16a our required propagator is then the integral over $(r_1, \beta_1), \cdots, (r_4, \beta_4)$ of the product of two chain propagators (see Eq. 86 for full expansion)

$$\mathscr{F}_{n_1}(r_2\beta_2; r_1\beta_1) \quad \text{and} \quad \mathscr{F}_{n_2}(r_4\beta_4; r_3\beta_3)$$

and one toron propagator with four interaction points:

$$\frac{1}{(2\pi h)^6} \sum_{t_1 \cdots t_4} \int \cdots \int d^3q_1 \cdots d^3q_4 \, \beta^{1-3} \, \delta(q_1 + q_2 + q_3 + q_4) \, \delta_{t_1 + \cdots + t_4, 0}$$

$$\times \Lambda_4(q_1 t_1 \cdots q_4 t_4)u(q_1)u(q_3)$$

$$\times \exp i \left[(q_1 \cdot r_1 + \cdots + q_4 \cdot r_4)h^{-1} + \frac{2\pi}{\beta} (t_1\beta_1 + \cdots + t_4\beta_4) \right].$$
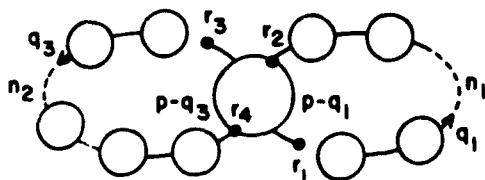
(a)
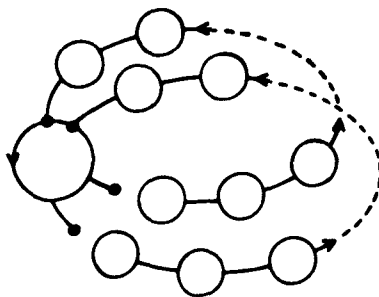
(b)

Figure 16

After multiplying all these functions together the integrations over the r's and β's yield delta functions which give the usual conservation of momentum and energy equations.   One finally obtains

$$(89) \quad \frac{1}{\beta} \frac{V}{(2\pi h)^3} \sum_{t_1 t_3} \int \int d^3 q_1 \, d^3 q_3 [-u(q_1)]^{n_1} [-u(q_3)]^{n_2} \Lambda_2^{n_1}(-q_1 - t_1 : q_1 t_1)$$

$$\times \Lambda_2^{n_2}(-q_3 - t_3 : q_3 t_3) \Lambda_4(-q_1 - t_1 : q_1 t_1 : -q_3 - t_3 : q_3 t_3).$$

The cases in which n_1 or n_2 are equal to zero are "exchange integrals" and require a special analysis which we shall not make here.

The reader can now see how to proceed with the calculation of a general diagram.   He will have little trouble in convincing himself that he should use the following rules:

(1) For each toron with m interaction points in the diagram, introduce a factor $\Lambda_m(q_1 t_1 ; q_2, t_2 ; \cdots ; q_m t_m)$ where $(q_1, t_1), \cdots, (q_m, t_m)$

are the amounts of momentum and energy lost at each interaction point.

(2) For each interaction line of momentum, q, introduce the factor $-u(q)$.

(3) Introduce a factor β^{l-I} where l is the total number of torons and I the number of interaction lines in the diagram.

(4) Integrate the product of the above factors over all momentum transfers and sum over all energy transfers (energy being transferred in quanta of magnitude $2\pi t/\beta$, t being an integer). The conservation laws are to be applied at each interaction point on a toron.

(5) Introduce a factor $V/(2\pi h)^3$.

(6) Introduce the combinatorial factor $(1/l!2^n)$ (number of ways diagram can be drawn) where l = number of torons and n is the number of independent paths along which momentum can be transferred.

The factor $V(2\pi h)^{-3}$ arises from the fact that the last delta function in dealing with momentum conservation in particle propagators is to be interpreted (see Eq. 23) as $V\delta_{p_1 p_2}(2\pi h)^{-3}$. The physical significance of the V is that all interactions depend only on relative coordinates. Hence in the configurational form of the partition function, the integration over the position of the last particle merely contributes the volume of the container.

The origin of the factor β^{l-I} is as follows. In the (r, β) representation of the grand partition function, the ith toron propagator of a complex diagram composed of l torons has the β containing factor $\prod_{i=1}^{l}(\beta/\beta^{n_i}) = \beta^{l-2I}$, since the total number of interaction points, $\sum n_i$, is twice the number of interaction lines I. The interaction lines represent isothermal interactions, both ends of the line being associated with the same temperature. Hence in the final β integrations, a factor β appears for each line, yielding a total factor β^I. When multiplied by the above β^{l-2I}, we obtain the β^{l-I} mentioned in rule 3.

In order to perform detailed calculations, one must have explicit expressions for the Λ's rather than their integral representations. Although the 4-fold integrations (83) are relatively straight-forward (at low temperatures they proceed in a manner similar to the usual Summerfeld method for integrals which appear in the perfect FD or EB gas) the required expressions are quite long except for the case $n = 2$. A detailed investigation of these integrals is contained in a forthcoming review of the statistical mechanics of an electron gas. Here we merely record a few asymptotic results for $\Lambda_2(-q, -t; q, t)$ (see reference 15).

In the Maxwell Boltzmann statistics

(90a) $$\Lambda_2(-q, 0; q, 0) = z\beta\left(\frac{2\pi m}{\beta}\right)^{3/2} \sum_{n=0}^{\infty} \frac{(-1)^n n! (q^2\beta/2m)^n}{(2n+1)!}$$

$$\sim z\beta\left(\frac{2\pi m}{\beta}\right)^{3/2}[1 + O(q^2)]   \text{as } q \to 0$$

(90b)

$$\sim \frac{4m}{q^2}\left(\frac{2\pi m}{\beta}\right)^{3/2} + O(q^{-4})   \text{as } q \to \infty.$$

If $t \neq 0$ and

(91) $$\Lambda_2(-q, -t; q, t) \sim \frac{4mz}{q^2 + (v/q)^2}\left(\frac{2\pi m}{\beta}\right)^{3/2}\{1 + O(1/q^2[1 + (v/q^2)^2])\}$$

(92) $$v = 2\pi m t/\beta,$$

when either $q^2 \gg 2m/\beta$ or $(\tfrac{1}{2}v/q)^2 \gg 2m/\beta$.

In the FD case as $\beta \to \infty$ for fixed Q and V

$$\Lambda_2(-q_1 - t; q, t) \to \frac{\pi m p_0}{2Q}\left\{4Q + [1 + (V + iQ)^2]\log\frac{[(V + iQ) + i]}{[(V + iQ) - i]}\right.$$

(93) $$\left. + [1 + (V - iQ)^2]\log\frac{[(V - iQ) - i]}{[(V - iQ) + i]}\right\}$$

where

(94) $$z = \exp - p_0^2\beta/2m;   V = \frac{2\pi t m}{\beta q p_0};   \text{and}   Q = q/2p_0.$$

It is easily shown from (93) that

(95) $$\Lambda_2(-q, -t; q, t) \sim \begin{cases} 4\pi m p_0(1 - V\tan^{-1}V^{-1}) & \text{as } Q \to 0, \\ \dfrac{4\pi m p_0}{Q^2}\left(\dfrac{2}{3} - V^2\right) & \text{as } Q \to \infty. \end{cases}$$

4. Application to an assembly of charged particles. We now apply the general formalism described above to the statistical mechanics of a gas of negative ions imbedded in a continuum of positive charge whose charge density is so fixed that the complete assembly is electrically neutral. Since our formalism is a systematic perturbation theory in which $\log Z_G$ is presented as an expansion in powers of the inter-particle coupling constant (e^2 in our case) it is best in the weak

coupling range, i.e. $e^2 \to 0$.   The other parameters which are necessary to describe our assembly are the particle mass, m; the particle density, ρ; $\beta = 1/kT$ and h.

Since the constant h is absent from the grand partition function appropriate for the high temperature classical limit, this function must depend only on the single dimensionless parameter which can be constructed from the remaining quantities, $\beta e^2 \rho^{1/3}$.   Hence a perturbation expression which is valid for small e^2 is equally valid for small β (high temperature) or small ρ (density) for fixed e^2.

In the ground state (i.e. $\beta \to \infty$, zero temperature) the parameter β disappears from various formulae.   The only dimensionless quantity which can be constructed from the remaining parameters is $me^2/h^2 \rho^{1/3}$. Hence in the ground state a perturbation expansion in e^2 is appropriate for high densities at any fixed e.

(a)   (b)
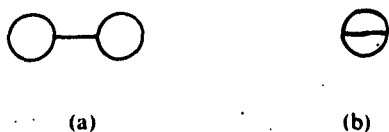
Figure 17

The above remarks imply that if we derive a perturbation correction to a perfect gas law which is a small coupling constant approximation, it is equally valid as a high temperature, low density approximation or a low temperature, high density approximation. .

To obtain the first correction to the perfect gas grand partition function we calculate the terms of lowest order in e^2.   The diagrams associated with terms of order e^2 have one interaction line.   They are exhibited in Fig. 17.   It turns out that in an electrically neutral assembly, all diagrams which can be decomposed into two disconnected diagrams by cutting a single interaction line (for example, Fig. 17a and 18(a) and (e)) vanish.   The diagram of Fig. 17b represents what is known as the lowest order exchange integral.   It was calculated many years ago and offers no difficulty.   We do not discuss it here since no special features of the systematic perturbation theory are required.

The next order terms are those proportional to e^4, those associated with diagrams with two interaction lines.   They are exhibited in

Fig. 18.   For reasons mentioned above, Fig. 18a and Fig. 18b contribute nothing to log Z_G.

(a)   (b)

(c)   (d)   (e)
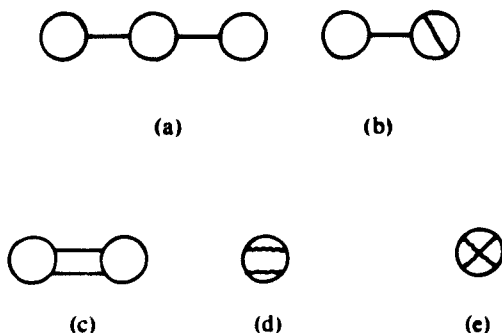
Figure 18

The contribution of 18(c) to log Z_G is (employing the rules of the last section)

$$(96) \qquad \frac{V}{4(2\pi\hbar)^3} \sum_t \int d^3q\, u^2(q) \Lambda_2^2(-q, -t; q, t),$$

where (see Eq. 45)

$$u(q) = e^2/2h\pi^2 q^2.$$

Note that when $t = 0$ in the MB statistics (Eq. 95)

$$(97) \qquad \Lambda_2^2 \sim z^2\beta^2(2\pi m/\beta)^{3/2} + O(q^2)$$

so that our required integral (96) diverges in the small q range.   No difficulty exists in the large q range.   When $t \neq 0$, $\Lambda_2^2 = O(q^4)$. Hence for small q when $t \neq 0$, $d^3q\, u^2(q) \Lambda_2^2 = O(q^2)\, dq$ and there is no divergence problem.   In the FD case (Eq. 95) Λ_2 is independent of Q as $Q \to 0$.   Hence the integral in (96) again diverges.   In summary, after working so hard to derive a systematic perturbation theory, we find that the first perturbation integrals diverge so that at first glance our work seems for nought.   Actually the divergence difficulty was known (in a somewhat different form) in the classical theory of electrolytes some forty years ago as well as in the FD case of an electron gas in a metal some thirty years ago.

Debye and Hückel avoided the divergence by employing another method of the calculation of the thermodynamic properties of electrolytes.   However, their method was appropriate only for very dilute

solutions and could not be extended to higher concentrations.   J. E. Mayer made the correct step to resolve the divergence difficulty in the MB case and Gell-Mann and Brueckner independently used the same idea in the FD case.

Suppose that instead of fretting over our troubles in the calculation of (96), we go on to the next order nonexchange contribution to $\log Z_G$, the ring of three interacting particles

$$-\frac{V}{6(2\pi h)^3} \sum_t \int d^3q \, u^3(q) \Lambda_2^3(-q, -t: q, t).$$

This term is even more divergent than (96).   However, the sum over all rings (Eq. 88)

$$(98) \quad \frac{V}{2(2\pi h)^3} \sum_t \int d^3q \{ \Lambda_2(-q, -t:q, t) u(q)$$
$$- \log [1 + u(q)\Lambda_2(-q, -t:q, t)] \}$$

is convergent.   For example, if in the MB case we examine the $t = 0$ term and approximate Λ_2 by $z\beta(2\pi m/\beta)^{3/2}$, we have

$$(99) \quad \frac{V}{2(2\pi h)^3} \int_0^x 4\pi q^2 \, dq \left\{ \frac{\alpha}{q^2} - \log\left(1 + \frac{\alpha}{q^2}\right) \right\}$$

where

$$(100) \quad \alpha = \frac{z\beta(2\pi m/\beta)^{3/2} e^2}{2h\pi^2}.$$

The above convergent integral has the value

$$(101) \quad \frac{2\pi^2 V \alpha^{3/2}}{3(2\pi h)^3} = \frac{2\pi^2 V}{3(2\pi h)^3} \left(\frac{ze^2 m}{h}\right)^{3/2} \left(\frac{2m}{\pi\beta}\right)^{3/4}.$$

Since the perfect gas contribution (1-toron contribution) to the $\log Z_G$ is (see Eq. 47) $zV/h^3(2\pi\beta/m)^{3/2}$, the total contribution of the noninteracting particle graphs plus ring graphs to $\log Z_G$, or to PV/kT is (see Eqs. 48 and 36)

$$(102) \quad \frac{PV}{kT} = \log Z_G = \frac{zV}{h^3(2\pi\beta/m)^{3/2}} + \frac{2\pi^2 V}{3(2\pi h)^3} \left(\frac{ze^2 m}{h}\right)^{3/2} \left(\frac{2m}{\pi\beta}\right)^{3/4}$$

while z and the density ρ are related through (Eq. 49)

$$(103) \quad \rho = \frac{z}{V} \frac{\partial \log Z_G}{\partial z} = \frac{z}{h^3(2\pi\beta/m)^{3/2}} + \frac{\pi^2}{(2\pi h)^3} \left(\frac{ze^2 m}{h}\right)^{3/2} \left(\frac{2m}{\pi\beta}\right)^{3/4}.$$

Here one is interested in z as $e^2 \to 0$.   In the limit

$$(104) \qquad\qquad z_0 = \rho \hbar^3 (2\pi\beta/m)^{3/2}.$$

The correction δz to this value when e is small but finite is obtained by substituting (104) into the second term on the right hand side of (103) and solving for the z in the first term on the right hand side (104).   One obtains

$$(105) \qquad z = (2\pi)^{3/2}\hbar^3(\beta/m)^{3/2}\rho\{1 - e^3\beta^{3/2}\rho^{1/2}\pi^{1/2} + O(\rho)\}.$$

Substituting this into (102) we find the Debye-Hückel equation of state

$$(106) \qquad\qquad P/kT = \rho\left\{1 - \frac{1}{3}\pi^{1/2}e^3\beta^{3/2}\rho^{1/2}\right\}.$$

The high pressure ground state energy of an electron gas is obtained by substituting (93) into (98).   As $\beta \to \infty$ $(T \to 0)$ the parameter

$$V = 2\pi t m/\beta q p_0$$

becomes a continuous variable even though t is discrete. . The summation with respect to t can be converted to an integral with respect to V.   Then (98) becomes (after letting $q = q'p_0$ and ignoring the prime on q' and allowing for two spin states by replacing $u(q)\Lambda_2$ by $2u(q)\Lambda_2$)

$$(107) \quad \frac{Vp_0^5\beta}{m(2\pi\hbar)^3}\int_0^\infty q^3\,dq \int_{-\infty}^{+\infty} dV\left\{\frac{e^2\Lambda_2(q,V)}{\hbar\pi^2 p_0^2 q^2} - \log\left[1 + \frac{e^2\Lambda_2(q,V)}{\hbar\pi^2 p_0^2 q^2}\right]\right\}.$$

The $\log Z_G$ is then, to the ring integral approximation,

$$(108) \qquad\qquad \log Z_G = \log Z_G^{(0)} + (107)$$

where $Z_G^{(0)}$ is the grand partition function of a perfect Fermi gas.

The internal energy is found by differentiating (108) with respect to β at constant $z = \exp \beta p_0^2/2m$; the density by differentiating (108) with respect to z at constant β.   For this purpose we substitute $p_0 = (2m\beta^{-1}\log z)^{1/2}$ into (108) before carrying out our differentiations.   The details of the differentiation are tedious but straightforward.   They have been given in some detail in the original paper of Montroll and Ward.   As in the classical case we assume that $z = z_0 + \delta z$ where z_0 is now chosen to be $\exp (\beta p_F^2/2m)$ (p_F being the Fermi momentum $\hbar(3\pi^2\rho)^{1/3}$.   Then the correction δz is found to

keep the density at p.   Now one can express the ground state energy (as $\beta \to \infty$) as

$$E = E_0(z) + \delta E(z)$$

$$= E_0(z_0) + \left\{ \frac{\partial E_0}{\partial z} \delta z + \delta E(z_0) \right\} + \cdots .$$

The first order correction to the free particle contribution to the ground state energy has two parts, one being the direct correlation energy evaluated at $z = z_0$ and the second being the change in the free particle energy due to the fact that z must be changed to yield the proper density.   One finally obtains the correlation energy, $[E - E_0(z_0)]$, to be

$$(109) \quad E_{\text{corr}} = \frac{-3h^2}{8\pi m\alpha^2 r_0^2} \int_0^{\alpha} q^3 \, dq$$

$$\times \int_{-\infty}^{+\infty} dV \left\{ \frac{e^2 \Lambda_2(q, V)}{h\pi^2 p_F^2 q^2} - \log\left[1 + \frac{e \Lambda_2(q, V)}{h\pi^2 p_F^2 q^2} \right] \right\}$$

where $(4/3)\pi p r_0^3 = 1$ and $\alpha = (4/9\pi)^{1/3}$.   This is exactly the Gell-Mann-Brueckner formula for the correlation energy per particle of an electron gas.   A detailed discussion of the integral is given in the Brueckner lecture notes of the 1958 École d'Été de Physique Théorique. Numerically Brueckner finds (in Rydbergs)

$$E_{\text{corr}} = -0.096 + 0.0622 \ln r_s$$

with $r_s = r_0/r_B$, r_B being the Bohr radius.

The physical idea behind the removal of the small q divergence is that each direct interaction between two particles is to be replaced by the sum of ── + ──O── + ──O──O── + $\cdots$, the direct interaction plus an interaction through an intermediate particle plus one through two intermediates, etc.   We examine the consequence of this idea in the classical limit.   We consider only the terms $t = 0$, since in our required limit only these terms led to divergences.   Then we should replace $u(q)$ by

$$(110) \quad u(q) - \Lambda_2(-q, 0; q, 0)u^2(q) + \Lambda_2^2 u^3(q) \cdots = u(q)/[1 + \Lambda_2 u(q)].$$

From this we can calculate an effective potential to replace the coulomb potential e^2/r.   This potential would be just the Fourier transform of (110)

$$(111a) \qquad \frac{e^2}{2h\pi^2 q^2} \int \frac{d^3 q \exp(iq \cdot rh^{-1})}{[1 + \alpha q^{-2}]q^2} = \frac{e^2}{r} \exp - \kappa r$$

where $1/\kappa$ is the so-called Debye length:

$$(111b) \qquad\qquad \kappa^2 = 4\pi\beta\rho e^2.$$

The factor exp $-\kappa r$ is the well-known Debye screening factor.

Now it can be shown in a systematic way, by rearranging diagrams in the cluster integral expansion, that the grand partition function can be expended in terms of cluster integrals involving the screened coulomb potential. Let us see what is involved in calculating in the classical limit the simplest of these (see Fig. 19). In the figure each

Figure 19

bond connecting our two 1-torons is the screened potential rather than e^2/r. We perform the calculation in position space. First we note that our two torons at the ends of the diagram shrink to a point in the limit $\beta \to 0$, since each toron has a circumference β. We also divide by $1/3!$ so that we can integrate freely over the β's at interaction points (see remark after Eq. 32). Note that the free particle propagator (19) approaches $\delta(r_2' - r_1')$ as $(\beta_2 - \beta_1) \to 0$. Hence all interaction points in Fig. 19 coalesce into one point and our required integral is

$$-\frac{1}{3!} \int_0^\infty 4\pi r^2 \left(\frac{e^2}{r} \exp -\kappa r\right)^3 dr = -\frac{4\pi e^6}{3!} \int_0^\infty r^{-1} \exp\left(-3\kappa r\right) dr$$

which diverges. We eliminated the divergence in one class of diagrams due to the long range character of the coulomb interaction (small momentum transfer) only to find that another class of divergences have appeared due to the behavior of the screened coulomb potential at short distances. Here we must be brave and consider the whole class of diagrams with two node points

which are known as "watermelons" in the classical limit and "ladders" in the quantum limit.   The nth of these is

$$(-1)^n \frac{4\pi e^{2n}}{n!} \int_0^\infty \frac{\exp(-n\kappa r)}{r^n} r^2 \, dr$$

so that the sum over all of them (starting with the third, the second merely being our old ring integral)

$$-4\pi \int_0^\infty r^2 \Big\{ \exp(-e^2 r^{-1} \exp -\kappa r) - 1 + \frac{e^2}{r}(\exp -\kappa r)$$
$$- \frac{e^4}{2r^2}(\exp -2\kappa r)\Big\} \, dr$$

which converges.   This type of collection of diagrams was first due to Morita, its application to the coulomb interaction problem by Abe. The collection of ring diagrams was first made by Montroll and Mayer and the application to the coulomb interaction problem by Mayer. We do not proceed further here to find the actual contribution of the watermelon terms to $\log Z_G$.

Summary. We conclude with a list of the main ideas involved in the perturbation theory of quantum statistics of interacting particles.

1. The theory starts with the Green's function form of the Bloch equation which is in turn transformed into an integral equation which is solved by iteration; the nth order iteration is proportional to the nth power of the coupling constant which characterizes the strength of the interparticle interaction.

2. A diagrammatic representation is introduced which makes it possible to identify any term in the perturbation expansion without long detailed formulae.

3. The logarithm of the grand partition function (from which all thermodynamic quantities can be calculated) `` expressed as a sum over all connected diagrams containing any number of interaction lines and particles.   This form can be characterized in the following manner.   The grand partition function is the sum over all possible elementary events on our (r, β) or (p, E) cylinder which involve any number of particles and quanta of interaction provided that the events are such that no free end exists on any particle or interaction quanta propagator lines and that all diagrams which represent the events are connected.   A weight z^n is given to events which involve n particles, every segment of a diagram is represented by either a free particle propagator or an interaction propagator.   The only elementary events are the creation and annihilation of particles or quanta

of interaction with energy and momentum being conserved during the occurrence of each event.   Actually one could start with these remarks as the basic postulates of statistical mechanics and derive all other results from them.

4. Finally, divergences occur in the evaluation of various cluster integrals which are associated with our diagrams.   These are removed by summing over various classes of diagrams and performing energy momentum transfer integrations after the summation is performed. This is the weak point of the theory as here presented.   One has to rely on physical plausibility rather than mathematical rigor to have confidence in the results.   It is not even clear that all divergences can be dealt with in this way; it just turns out that in the weak coupling limit, the first few terms in the systematic expansion of thermodynamic functions seem to work out well.   One optimistically continues, hoping that all is right with the world.

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